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THE DISTRIBUTION OF MINERAL DATES IN TIME AND SPACE

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ABSTRACT. Most igneous and metamorphic mineral dates indicate times of rock cooling, the terminal events of crustal adjustment. Accordingly, the distribution of mineral dates in time indicates the periodicity of such events, and the distribution in space indicates the geometry of their occurrence. By this we may test the validity of such concepts as "orogenic periodicity", "cyclic orogeny", and "continental accretion".

A plot of mineral date abundance against age shows that crustal adjustments are periodic and roughly cyclic. Intervals for which abundant mineral dates have been preserved are about 175 to 250 million years in length, with cycles of about 350 to 500 million years. Intervals of date abundance fall in the ranges: -2710 to -2490 m.y., -2220 to 2060 m.y., -1860 to -1650 m.y., -1480 to -1300 m.y., -1100 to -930 m.y., -620 to -280 m.y., and -120 to the present.

Mineralogenic events of very different ages are commonly recorded in the same area, not infrequently in the same rock. Large areas, however, can be characterized by the mineral dates of the last interval of mineralogenic activity by which they were seriously effected. In North America these mineralogenic provinces show a crudely concentric pattern, younger dates outward. Similar arrangements have not been found in other continents.

INTRODUCTION

The temporal distribution of crustal adjustment and the geometry of unstable areas have long been topics of geologic discussion and hypothesis. To utilize mineral dates in resolving these questions it is first necessary to decide what events they record, which mineral dates are applicable to the study of large-scale crustal adjustment, and to what extent we may rely on existing mineral dates. After choosing criteria for the selection and evaluation of dates it is possible to tabulate and plot them according to their time and space distribution. Naturally we must satisfy ourselves that the sample is sufficiently large and areally distributed to be representative of a region. Finally, it will be possible to examine the degree of temopral and spatial order, check the statistical significance of this order, and use it as a test of geologic concepts. If our conclusions are valid it should be possible to predict the time and space distribution of mineral dates as yet undetermined.

ACKNOWLEDGMENTS

The fund of mineral age data upon which this paper is based is the contribution of many researchers in laboratories all over the world. The compilation of this material has been significantly aided by the work of Holmes and Cahen (1957) and Gheith (1958a, 1958b). Correspondence and discussion with H. W. Fairbairn, Massachusetts Institute of Technology, A. H. Lang, Geological Survey of Canada, Leon Silver, California Institute of Technology,

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THE EVENTS RECORDED BY MINERAL DATES

Most geologic events involve the growth or regrowth of crystalline minerals. Uplift and erosion, sinking and sedimentation, faulting and folding, all trace their origin to physical-chemical adjustments which, through magmatization or metamorphism, ultimately require mineral crystallization.

Where a crystal contains atoms which disintegrate spontaneously, the chemical composition of the mineral changes as a function of time, almost independently of environment. The altered atoms, thus formed, may or may not be accommodated by the crystal. Some are able to escape as soon as formed (radon), some escape only after a threshold concentration has been achieved (argon in feldspar?), and others can accumulate almost indefinitely. As long as they do not escape from the crystal in which they were formed their abundance is a measure of the time elapsed since crystallization.

If, after crystallization, a change in physical environment requires recrystallization to the same or a different mineral, most of the daughter atoms not required by the new form will be excluded. The abundance of daughter atoms, then, tells us how much time has elapsed since the crystal in question was capable of expelling them. Unfortunately we do not know the limiting physical-chemical conditions which control the retention or expulsion of daughter atoms. Comparative studies of different age-dating methods (references below) show us that the same environment which brings about the removal of daughter atoms from one element ratio, or from one mineral, is not necessarily effective in removing a different daughter element, or in removing the same element from an adjacent mineral of a different species (M.I.T., 1958a; Grunenfelder, 1958; Tilton, et al., 1958a, b; Aldrich, 1958). It is this overlap in retention stability that makes it possible to obtain the date of more than one geologic event from the same rock.

When the environment of a crystal requires the expulsion of daughter atoms, does the crystal necessarily undergo rapid and total cleansing so that its "age" is neatly reestablished as that of the time of cleansing? Or is it possible that only a portion of the unaccommodated atoms are expelled, leaving the crystal with an intermediate "age value" that does not date any event? Obviously a composite crystal, portions of which have grown at measurably different times, will not yield significant age data unless the different portions can be analyzed individually. If the parent-daughter isotope ratios in a rock have been affected by gradual daughter-escape, partial daughter-cleansing, or composite crystallization, different mineral species, and different radiogenic isotope ratios within those minerals would not be expected to yield the same "age". However, many cases of date concordance have been found, and these must record physical events in the history of the earth's crust.

To utilize mineral dates geologists must make assumptions as to the nature and circumstances of the causal event. This event may have been crystallization

from a melt, metamorphism, or deposition from an aqueous fluid. Since these processes may require millions of years for completion, and may more or less continuously accompany tectonic instability over still longer intervals of time, the mineral dates which are preserved represent only the final achievement of crystal stability, the terminal cooling. This final stability is achieved individually by each crystal, and due to the heterogeneity of orogenic belts, and the continual structural dislocation within them, mineral dates representing the entire history of a mineralogenic province may be preserved. The spread of mineral dates ascribed to a mineralogenic epoch may or may not represent the entire interval of crustal instability.

THE SELECTION OF MINERAL DATES SIGNIFICANT TO THE STUDY OF CRUSTAL STABILITY

In dating intervals of crustal adjustment we are most concerned with the crystallization of deep-seated igneous and metamorphic rocks. Micas, potassium feldspar, and accessory minerals such as zircon and monazite are primary constituents of such rocks and contain one or more naturally radioactive elements. Pegmatites and associated hydrothermal veins which are satellitic to centers of magmatization or metamorphism should yield dates no older or younger than the active life of their source. These contain micas, potassium feldspar, and a variety of primary uranium and thorium minerals. Medium- to low-temperature vein and replacement hydrothermal deposits, as well as supergene deposits, may occur in areas marked by crustal stability, and therefore do not appear to be necessarily related to fundamental crustal adjustment. Some mineralogenesis in stable regions, however, appears temporally related to distant crustal adjustment (Cummings, 1955). Uranium mineralization on the Colorado Plateau during the deformation of the Rocky Mountains is one example.

A table of mineral dates is included as an appendix. This table is designed to include every locality for which a mineral date, attributed to fundamental crustal adjustment, has been determined by the use of methods and materials currrently regarded as reliable. Where several similar dates have been obtained for materials from one locality, more than one representative date is presented.

The dates have been classified as either *confirmed* or *tentative*. *Confirmed* dates are based upon corroborative determinations by different methods, materials, or samples. *Tentative* dates are those based upon a single determination, upon several highly discordant ones, or upon unsatisfactory or unknown methods or materials.

Concordant uranium-thorium-lead isotope dates and lead 206/207 dates for medium- to high-temperature minerals, rubidium 87/strontium 87 dates for low-calcium minerals, and potassium 40/argon 40 dates for micas and young ($<$100m.y.) potassium feldspar are considered to be reliable and significant. Dates determined by non-isotopic chemical analysis, common lead, helium, crystal damage, and lead-alpha methods, while frequently correct and useful as confirmations, are not considered reliable by themselves. Dates determined for older feldspars, secondary minerals, mineraloids, total rock, or sedimentary materials are likewise, by themselves, either unsatisfactory or unapplicable. Dates for which the mineral has not been given have generally been

omitted. To make the dates directly comparable they have been adjusted to the decay constants currently used by North American laboratories (Wetherill, 1957; Aldrich, et al., 1956a).

A spread of dates for a given locality may represent a sequence of closely spaced mineralogenic events, a difference in response to the same event by different minerals or elements, a difference in response to post-crystallization environment by different minerals, elements, or different crystals of the same mineral, or a lack of analytic precision. Thus, when we wish to consider individual localities in terms of representative dates there is no uniquely satisfactory or entirely objective procedure for generalizing the data. Where an analyst or reviewer has published a "preferred date" the preference has generally been followed and acknowledged. For a pair of determinations by different methods the average is used. For a pair of determinations on different materials by the same method the higher value is used. Where applicable, a superior method or a more recent determination is given preference. Where more than two determinations must be considered, those dates forming the most significant cluster are averaged. The method of generalization employed is indicated by a suffix attached to each composite date given in the table.

THE VALIDITY OF MINERAL DATES

Attempts to measure mineral age began soon after the discovery of natural fission (Marble, 1954, p. 3). During each decade since then analysts have discarded most of the age determinations made in the preceding one. Certainly many of the dates used in this paper are destined for revision, but generalizations based upon groups of dates have suffered a lower mortality rate than have the individual age values. In 1927 Holmes and Lawson presented a time scale of which the post-Cambrian portion differs little from that in use today. In 1932 Ellsworth showed that uraninites of the Grenville orogenic province were about one billion years old and much younger than those of the adjoining Keewatin province. At that time his conclusions differed from common geologic thought, but many subsequent determinations by improved methods have only confirmed and complemented his discovery.

THE STUDY OF MINERAL DATES ON GRAPHS AND MAPS

Plots of mineral date abundance against age.—In figure 1 mineral ages are plotted along the abscissa. Time is subdivided into intervals of ten million years, and the number of mineral date localities tabulated for each interval is plotted in histogram form parallel to the ordinate. Both *confirmed* dates (represented on the graph by solid squares), and *tentative* dates (represented by open squares) are plotted for the individual continents, but only the *confirmed* dates are plotted for the earth as a whole. The histograms are supplemented by a curve which draws attention to the date clusters. This curve is constructed by adding 4 vertical scale units for each date falling in the time interval in question, two vertical units for each of those falling in the two adjacent intervals, one unit for each of those in the four next closest intervals, and one-half for each in the next closest eight intervals. The area beneath the *confirmed* curve is shaded, whereas the curve representing *confirmed* plus *tentative* dates is

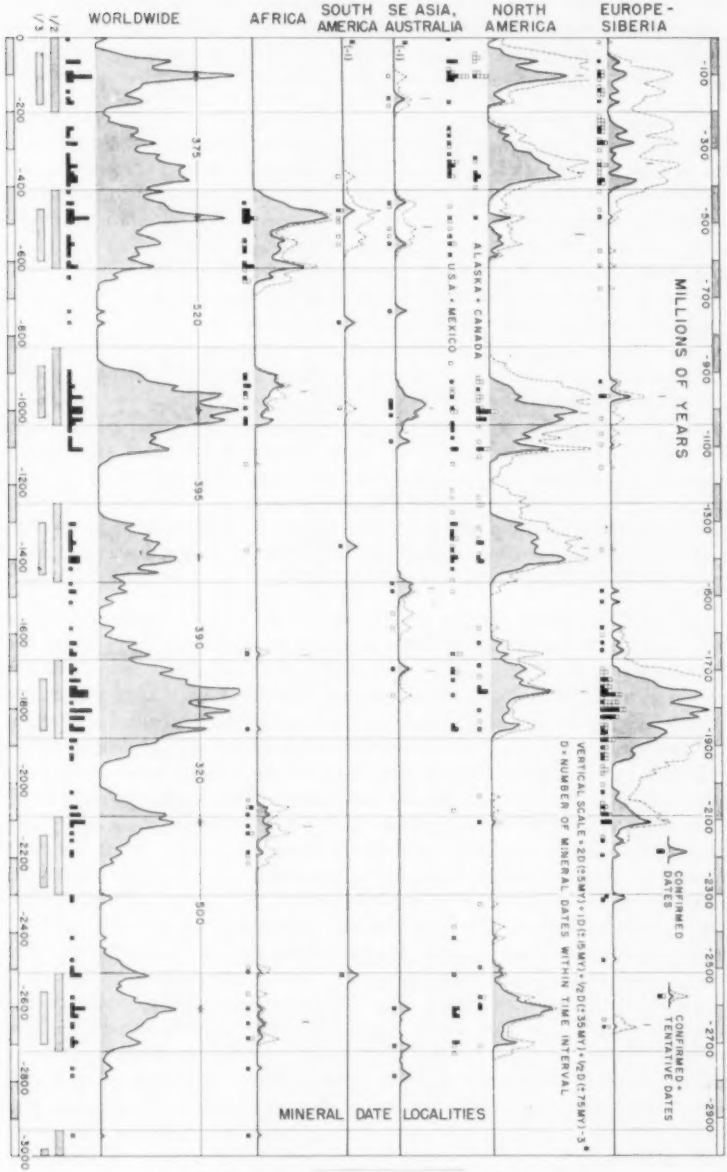

Fig. 1. Mineral date abundance plotted against age.

dashed. The three lowest vertical scale units are subtracted from all of the graphs except those for Southeast Asia—Australia, and South America, for which only one scale unit has been subtracted. The single date from Antarctica was included with Southeast Asia and Australia.

Sample representativeness.—If a coordinate grid were superimposed upon a map of North America and a mineral age determination were made for the closest appropriate material to each grid intersection the representativeness of the data would depend only upon the coordinate interval. The selection of material for mineral dating, however, has depended upon proximity to laboratories, the location of economic mineral deposits, roadcuts, and other man-dependent variables. As a result the number of determinations reported for some small areas and individual localities is out of proportion to their areal significance. In attempting to minimize this effect we have treated each mineral district or township as a single locality. The *area-compensated* graph for North America (fig. 2) is a further attempt to minimize the effect of disproportionate mineral distribution. To construct this graph North America was divided according to coordinates of longitude and latitude (fig. 3). Each grid area was then treated as a locality and one or more representative dates were selected according to the same criteria described previously for individual localities. Another check of sample representativeness was made by dividing North America along the geologically arbitrary United States-Canadian border (fig. 1). The marked agreement of both portions with the *area-compensated* graph for the entire continent shows that the date sample is representative.

It could be argued that the crystallization of a particular mineral species, or of minerals of a particular element, has not necessarily been distributed representatively through geologic time, and that therefore the respective mineral dates represent only those adjustments involving particular minerals or elements. To investigate this possibility the age values for each locality were tabulated according to method and mineral used. Where several determinations by the same method and material were available for a single locality they were compounded by the previously explained method. This treatment involves the use of many individual determinations and therefore produces greater dispersion on the distribution graph. In figure 2 there are separate plots for potassium-argon, rubidium-strontium, and a composite of uranium-thorium-lead method dates. The latter graph is divided into five histograms: (A) concordant uraninite determinations, (B) lead 206/207 determinations for uraninite, (C) concordant uranium-thorium-lead determinations for zircon, monazite, xenotime, allanite and other accessory minerals, (D) determinations by lead 206/207 for the accessory minerals, (E) determinations by the common lead method, lead-alpha method, non-isotopic chemical analysis of uranium and thorium minerals, and the isotopic analysis of pitchblende. Although there is a marked absence of uranium dates at about 350 m.y. and an absence of mica dates at 2100 m.y., the graphs for the different methods and materials show great similarity in date distribution. This coincidence indicates that radioactive mineral dates are representative of deep-seated mineral genesis as a whole.

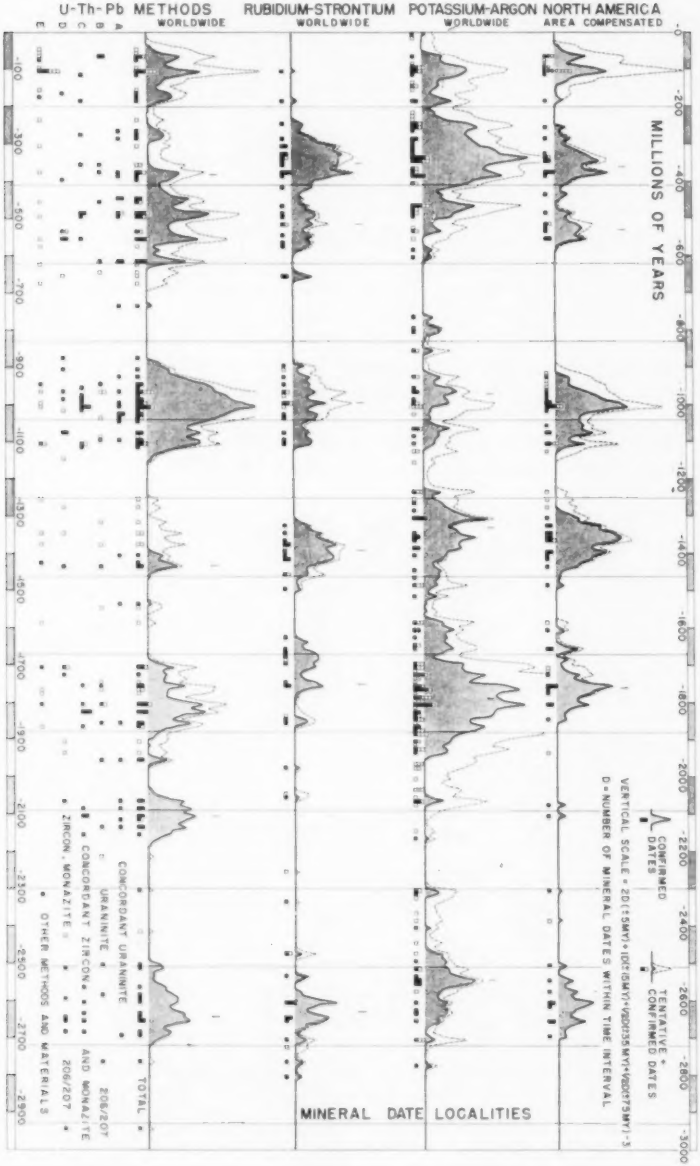

Fig. 2. Mineral date abundance plotted against age.

Finally consider the distribution of mineral ages with depth. In a crustal belt of recurrent mineral genesis (an orogenic belt) crystals of zero age are continuously or spasmodically being formed at all depths. Some crystals which cooled at great depth are carried toward the surface by structural dislocation, others by erosion and uplift. Processes of fusion, solution, and metamorphism that continuously re-establish mineral ages during the active life of the belt are increasingly important with depth. The surface rocks may contain mineral ages representing many or all of the past mineralogenic events of the area, while at great depth all minerals may bear the age of the most recent mineralogenic event. Thus, deeply eroded terranes like the Grenville orogenic province and the Pacific batholithic belt are relatively uniform in mineral age, whereas at Sudbury and in New England, where variably metamorphosed rocks are cut by many small intrusions, a wide spread of mineral ages has been preserved. The younger the terrane, the smaller the chance that it has been eroded to its mineralogenic roots; thus, the dispersion of mineral ages in recently unstable provinces should, all other factors neglected, be greater than in more ancient terranes. The Precambrian mineralogenic intervals can be expected to correspond more closely to the closing phases of orogeny, whereas post-Cambrian dates tend to represent the entire span of crustal instability.

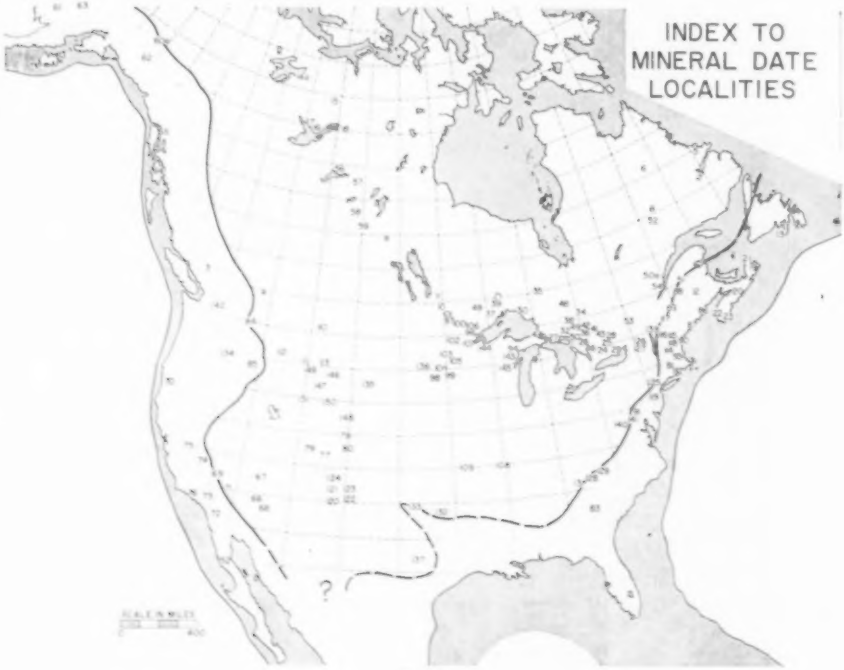

Fig. 3.

Mineral date provinces in North America.—Figure 3 locates the tabulated mineral dates for North America. Figure 4 shows the regional lineaments and structural grain of North American Precambrian rocks, as abstracted from the literature. The dotted lines indicate the apparent boundaries of Precambrian structural provinces. In constructing figure 5 we have sought a coincidence between these apparent structural boundaries and those of the mineral date provinces. The patterns by which the different provinces are distinguished are diagrammatic extrapolations of the structural patterns indicated by figure 4.

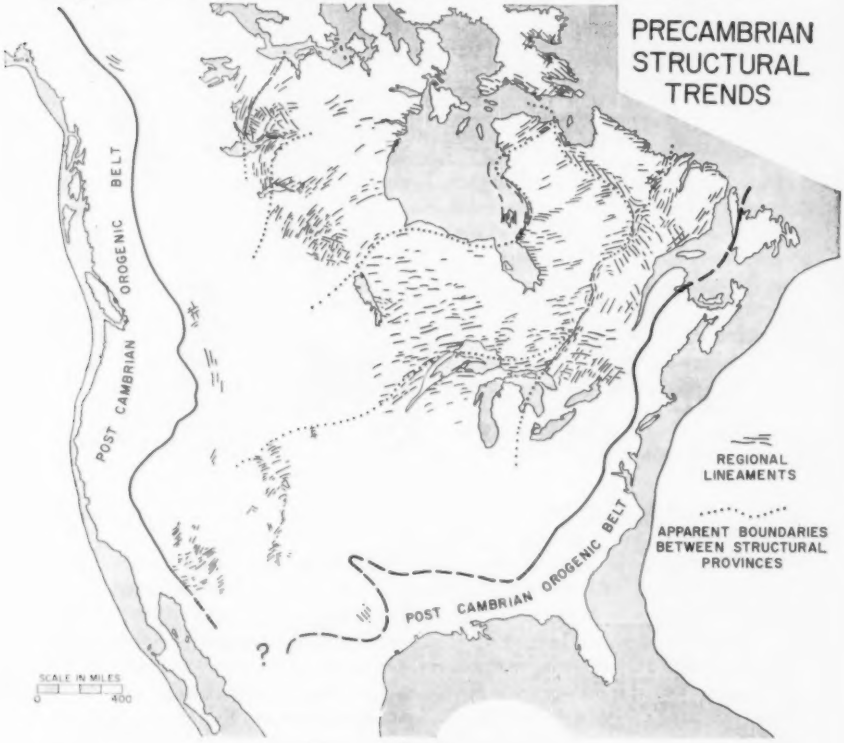

Fig. 4.

In figure 5 the mineral date localities of North America have been divided according to the abundance intervals which appear in figure 1. The intervals are designated by the letters A to G, younger to older. The distribution of mineral dates combined with considerations of regional geologic structure serves to define the mineral age provinces. Each province is characterized by the spread of dates representing the last widespread interval of orogenic mineralogenesis by which it was severely effected. Thus, the Pacific margin province is labeled 0-150, the Atlantic margin province 250-550, and the Grenville orogenic province 950-1100. Other provinces are characterized by the intervals 1250-

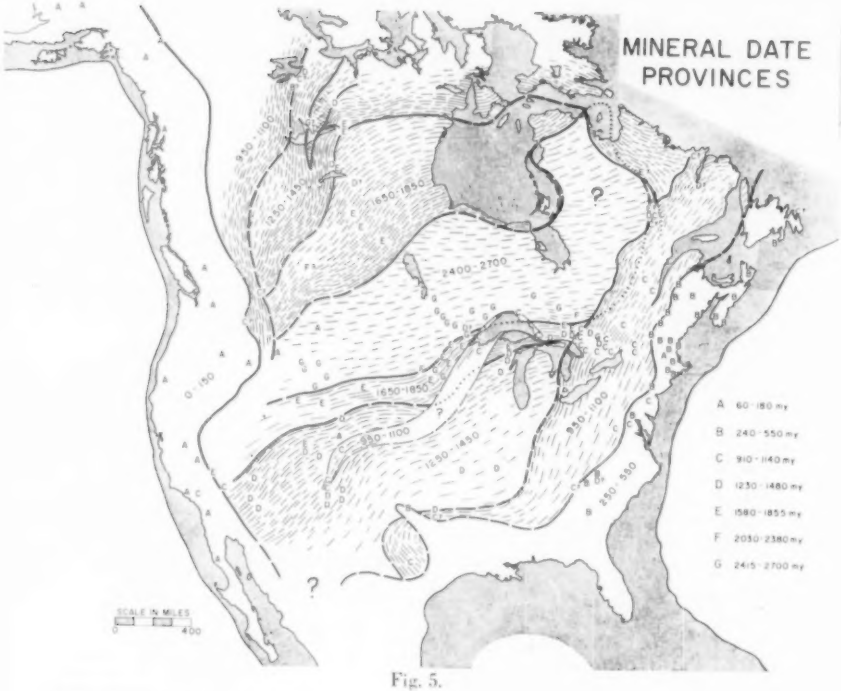

Fig. 5.

1450, 1650-1850, and 2400-2700. The complete spread of dates assigned to the respective intervals is given in the legend.

The absence of mineral dates from the Hudson Bay region, most of the Ungava Peninsula, the arctic islands, and much of south-central United States makes it impossible to present anything but a speculative working hypothesis.

Distance from continental escarpment plotted against age.—Figure 6 is a graphical demonstration of the observation made by J. Tuzo Wilson (1949) and others that the mineral age provinces of North America are progressively younger as they approach the present continental margin. In the graph the assigned age for each locality is plotted along the abscissa and its minimum distance inland from the continental escarpment is plotted parallel to the ordinate. The points define a diffused but definite trend toward greater age with greater inland distance. Part of the point scatter can be attributed to the tendency to seek out exceptionally young intrusions in older terranes and exceptionally old gneisses in younger provinces.

GEOLOGIC CONCEPTS IN THE LIGHT OF MINERAL DATE DISTRIBUTION

Episodes.—In 1958 Hurley (p. 1) wrote:

> The remarkable appearance of certain age values that occur in almost every continent has raised considerable speculation on the possible reasons behind these

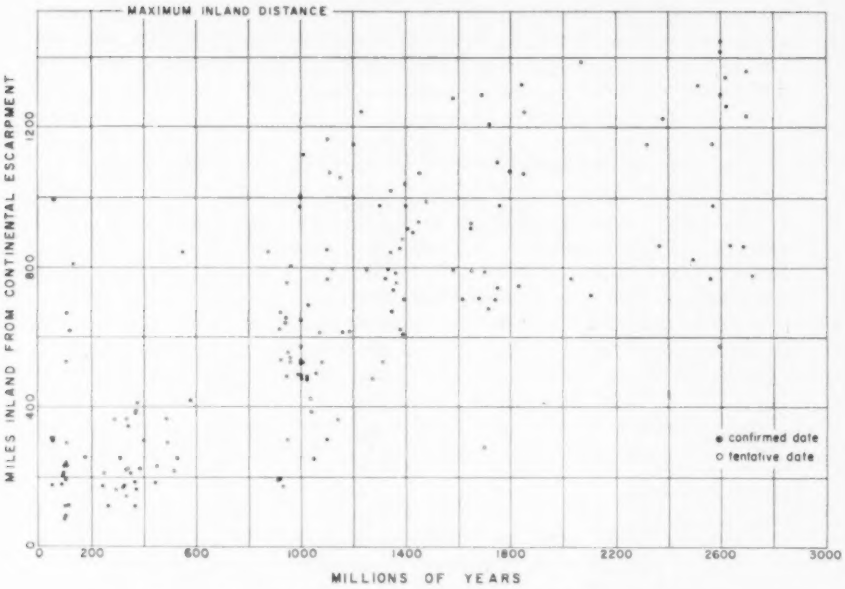

Fig. 6. Distance from continental escarpment plotted against age.

> world-wide orogenic events. Although not definitely proven to be the rule yet the evidence is becoming quite strong that these values are truly prominent points in time on a global scale.

And again (p. 2):

> The 2600 m.y. age has now appeared in Ontario, Quebec, the Northwest Territories (Yellowknife belt), Karelia, south and central Africa, India, Australia, and finally Brazil. The 1700 (± 100) m.y. is appearing in northern Manitoba, south Greenland, central Fennoscandia, the metamorphic belt involving the Huronian section of the Great Lakes region extending from the Sudbury district into Minnesota, at least parts of Labrador, India, central Africa, and the northern territories of Australia. Similar statements may be made regarding the typical Grenville age of about 1000 m.y., and the typical latest Precambrian age in the vicinity of 500 m.y.

Episodes of mineral date abundance, indicative of terminal crustal adjustment, comprise intervals of 160 to 340 m.y. (figs. 1, 2). Such age spreads are considered to be geologic rather than analytical (Fairbairn, 1958). The interval during which a given crustal belt has been unstable can, and probably does, far exceed the interval for which abundant dates have been preserved. For example, the Pacific margin batholithic belt, yielding Mesozoic ages, was already active in the Paleozoic, and the Appalachian orogenic belt, yielding predominately mid-Paleozoic ages, has its origin in the Precambrian.

Figure 1 shows the following intervals of mineral date abundance: 0 to −120 m.y., −280 to −620 m.y., −930 to −1100 m.y., −1300 to −1480 m.y., −1650 to −1860 m.y., −2060 to −2220 m.y., −2490 to −2710 m.y., and −2940 + m.y. These intervals are 120+, 340, 170, 180, 210, 160, 220, and 60+ million

years in length and together comprise 45 percent of the past 3 billion years. Table 1 shows the percentages of mineral dates which fall into these intervals. The average duration of the complete intervals is 240 m.y. with a standard deviation of 60 m.y.

TABLE 1

The Occurrence of Mineral Dates in Intervals of Abundance

	dated localities	confirmed + tentative	dated localities	confirmed
Europe-Siberia	146	70%	62	69%
North America	177	86%	98	94%
N. A. (area compensated)	109	88%	81	94%
SE Asia-Australia	23	70%	15	73%
South America	11	91%	3	—
Africa	56	82%	39	90%
Worldwide	413	78%	218	84%
Potassium/argon	231	67%	130	76%
Rubidium/strontium	86	86%	71	90%
U-Th-Pb methods	160	81%	107	86%

Table 2 lists the peaks of mineral date abundance indicated in figures 1 and 2. Mineral date interval B (see fig. 5) is indicated by two peaks, B and B′.

TABLE 2

Peaks of Mineral Date Abundance

	A	B′	B	C	D	E	F	G
Europe-Siberia	—	345	—	965	—	1800	2105	(2650)*
North America	100	365	530	1010	1370	1755	(2105)*	2605
N.A. (area compensated)	105	360	530	1005	1360	1760	(2090)	2605
SE Asia-Australia	(165)	—	510	995	(1475)	(1700)	—	(2695)
South America	—	—	475	—	(1365)	—	—	(2515)
Africa	—	—	485	950	—	(1655)	2115	(2640)
Worldwide	105	365	485	1000	1395	1785	2105	2605
Potassium/argon	105	335	470	970	1330	1790	—	2545
Rubidium/strontium	(105)	350	515	995	1390	1750	—	2630
U-Th-Pb methods	105	360	490	1005	1430	1815	2105	2645

* parentheses indicate a very small number of dates.

The average peak values (excluding those in parentheses) for the five continental areas are 105 m.y., 352 m.y. (standard deviation 12 m.y.), 500 m.y. (s.d. 20 m.y.), 980 m.y. (s.d. 25 m.y.), 1360 m.y., 1780 m.y. (s.d. 20 m.y.), 2110 m.y. (s.d. 5 m.y.), and 2605 m.y. Omitting B′, the intervals be-

tween these peaks are 395 m.y., 480 m.y., 390 m.y., 410 m.y., 332 m.y., and 493 m.y., giving an average interval of 417 m.y. (s.d. 47 m.y.). Very similar values can be obtained for each of the dating methods.

The existence of date abundance intervals does not necessarily mean that mineral growth has been episodic. These could result from an episodic redistribution in the extent of earth-wide mineralogenesis. By analogy, shoreline terraces are dated by the terminal activity of waves prior to a change in their space of activity. The waves have worked continuously, but the terrace levels that they left behind are evidences of an episodic earth history.

Cycles.—Since the intervals between peaks of date abundance average 417 m.y. the distribution of mineral dates has been compared with a hypothetical 420 m.y. cycle in which 210 m.y. intervals of mineral date abundance alternate with like intervals of mineral date scarcity. Except for the mid-Paleozoic mineralogenic interval (B′) found in the northern hemisphere, the distribution of dates agrees well with the cycles. The 210 m.y. half-cycles are indicated on figures 1 and 2 by vertical coordinates, and the intervals of greater mineral date abundance are shown as solid bars at the bottom of figure 1. Table 3 shows the percentages of dates which correspond to this cyclic pattern.

TABLE 3

The Cyclic Occurrence of Mineral Dates in Intervals of Abundance

	dated localities	confirmed tentative	dated localities	confirmed
Europe-Siberia	146	58%	62	60%
North America	177	71%	98	73%
N.A. (area compensated)	109	72%	81	73%
SE Asia-Australia	23	70%	15	67%
South America	11	82%	3	—
Africa	56	75%	39	85%
Worldwide	413	67%	218	71%
Potassium/argon	231	57%	130	59%
Rubidium/strontium	86	63%	71	61%
U-Th-Pb methods	160	74%	107	76%

By comparing the distribution of mineral dates with fixed cyclic intervals it is possible to investigate its statistical significance in the same manner as the flipping of a coin. Where p is the probability of occurrence of an event on a single trial, the Probability (P) that the event will occur at least r times in the course of n independent trials is:

$$P > r = \sum_{i\,0}^{i\,n-r} = \frac{n'}{i'(n-i)'} p^{n-i} q^{i} \qquad \text{(where } q = 1-p\text{)}$$

Considering each mineral date as a single trial, the chance of its falling into a

set of alternate intervals representing half of geologic time is one in two ($p = \frac{1}{2}$). The probability (P) that 71 percent of the 218 worldwide confirmed mineral date localities should give dates falling into the same set of intervals is less than 1×10^{-12}. Similarly, the probability for confirmed North American dates is about 1×10^{-8}, for European-Siberian 1×10^{-5}, and for African 1×10^{-6}. Similar calculations can be made setting p equal to 1/3, as suggested by the short bars in the lower part of figure 1.

If intervals of mineral date abundance are cyclic, they indicate a cyclic withdrawal of large portions of the earth's crust from active igneous and metamorphic mineralogenesis, a cyclic phenomenon quite different from that treated by Stille (1936) and Umbgrove (1942). The orogenic cycles which Stille, Umbgrove, and others recognized in the post-Cambrian record are events of a much smaller magnitude than those considered in this paper. The possible existence of long cycles in the earth's orogenic history has been suggested by many authors. Veining Meinez (1934, p. 531) writes:

> It is rather probable that in this whole phenomena we have to distinguish between currents of two sizes, a smaller one responsible for the different periods of tectonic activity, and a larger one taking place over the entire depths of the mantle which, at greater intervals than the first, would bring about the periods of especially strong tectonic activity (occurring at intervals of some 150-250 m.y.).

Gill (1955), when he spoke of 20 to 30 Precambrian orogenies, must have had in mind intervals similar to those of Veining Meinez. Cummings (1955) concluded that the active life of an orogenic belt is about 500 m.y. Holmes (1948) appears to have had in mind cycles of about 300 m.y. Griggs (1939) suggested a mechanism for producing orogenic cycles of about 560 m.y. in a given area, and M.I.T. (1958b) observes that orogenic belts develop over a period of 200 or more million years.

The concepts of periodic and cyclic orogeny to which Gilluly (1949) and Rutten (1949) objected concerned relatively short intervals of orogenic activity alternating with relatively long periods of quiescence. Their objections were not in conflict with the views of periodists such as Holmes, who wrote in 1932 (p. 186): "The testimony of geology is that compression seems always to have been more or less active somewhere or other in the world, periodicity being a matter of climaxes in particular regions heralded by crescendoes and followed by diminuendoes." Gilluly (1949, p. 588) says: "Of course I do not contend that intense crustal deformation has been either continuous or ubiquitous. Doubtless there have been variations in the rates from the statistical average, and perhaps present conditions deviate from the average in one direction or the other."

The concept of mineral date provinces and their meaning.—Following Ellsworth's (1932) pioneer use of mineral dates to distinguish the Grenville and Keewatin provinces, a succession of writers has attached characterizing mineral ages to "orogenic belts." In 1945 Holmes compared supposed intervals of North American orogeny with dates to the orogenic belts of south and central Africa and compared this succession of dates with supposed successions of orogeny in North America, Europe, and India. In 1949 J. Tuzo Wilson began using the age subdivision of the Canadian shield as evidence of "continental accretion." During these same years the existence of a Pacific batho-

lithic belt with mineral ages of –100 ± 30 m.y. and an Appalachian belt of –240 to –500 m.y., long suspected by field geologists, were confirmed by mineral dating.

In 1955 and again in 1957 Holmes and Cahen proposed a sequence of orogenic intervals for Africa. In 1955 Holmes expanded on his earlier time and space subdivision of India and Ceylon according to belts of Precambrian orogeny. In the Symposium on Precambrian correlation and dating held by the Geological Association of Canada in 1955 Derry, Gill, Cummings, and others amplified the mineral age subdivision of the Canadian shield.

In 1956 Tugarinov used mineral dates to subdivide the various Precambrian shields of the world according to successive belts of mountain building. In 1958 Gerling characterized the Precambrian orogenic belts of the Soviet Union by mineral dates, Goldich reported mineralogenic epochs for the Lake Superior region, Davis recognized an areal distribution of age "belts" in North America, and Hurley and Fairbairn reported the wordwide occurrence of "suspiciously similar dates."

Thus, in the past three decades, in each of the continents, clusters of mineral ages of areal significance and perhaps worldwide coincidence have been found. In 1956 J. Tuzo Wilson wrote (p. 550): "From the results now attainable it is quite apparent that the ages and lead isotope ratios found for any one area tend to be uniform but that they differ markedly from one geologic province to another. This regularity is much greater than had been anticipated . . ."

The picture, however, is not a simple one, for just as Tertiary intrusions are found well within the continent, rocks a billion years old intrude still older Precambrian terranes of Colorado, Minnesota, and Ontario. In the opposite regard each of the mineralogenic provinces preserves within it at least a few crystals which retain the ages of still more ancient mineralogenic events. Such examples of igneous rejuvenation and relicts from past epochs do not invalidate the concept of dated mineralogenic provinces, but they do indicate that old sialic crust is not immutably stable and that many orogenic belts are founded upon still older continental rocks.

Recently mineral ages of a billion years and more have been discovered on the coast of Labrador (Lang, 1958), in eastern Newfoundland (M.I.T., 1958a), in New Jersey (Davis, 1958b), near Baltimore (Tilton et al., 1958b), and in southern California (Larsen, see Faul, 1954; Davis, 1958a, Wasserburg, 1959) each within a relatively short distance of the present continental margin. This evidence is in direct conflict with the hypothesis of *continental accretion* (Wilson, 1949, 1950, 1956). It is not in conflict, however, if we attribute the concentric arrangement of mineralogenic provinces to a gradual withdrawal of crustal instability from the continent's interior. By this explanation the continent has not grown, but the portion of it involved in mineralogenesis has gradually decreased.

The distribution of mineral dates in other continents not only fails to support the hypothesis of accretion, but shows little evidence of an orderly withdrawal of instability from the continental centers. In Eurasia Precambrian terranes border both the Arctic and Indian oceans while mineral provinces of Paleozoic to Tertiary age extend through the heart of the continent. The min-

eral date map of Australia (M.I.T., 1958b, p. 94) locates the oldest dates near the ocean and younger dates in the continent's interior. The mineral date map of Africa (Holmes, see M.I.T. 1958b, p. 118) shows little relation between age and interior distance. And in South America Precambrian terranes extend to the coast in several places.

Orogenic rejuvenation.—Have continental areas, once stable for hundreds of millions of years, remobilized to participate in widespread magmatization and metamorphism? Areas with complex histories, such as Yellowknife (Henderson, 1955), Lake Superior (Goldich, 1958), Sudbury (M.I.T., 1958a), the Appalachian Piedmont (Tilton, et al., 1958a, b; Grunenfelder, 1958), Kouvo, Finland (Davis, 1958), the southern Ukraine (Vinogradov, 1956), and Karelia (Gerling, 1957) retain mineral dates from two or more widely separated times. Either these areas underwent periodic rejuvenation or significant portions of their mineralogenic record have yet to be discovered. For example, the Grenville orogenic province became stable about 1000 m.y. ago, and the adjacent Appalachian orogenic province 250 to 300 m.y. ago. Since the Appalachian province also participated in the Grenville orogeny, did it also stabilize 1000 m.y. ago and later remobilize, or was it continuously unstable until late Paleozoic time? If the area was continuously active it is difficult to explain the preservation of –900 to –1100 m.y. dates, considering the almost total absence of –550 m.y. to –900 m.y. dates.

If continents have neither grown nor become progressively stable toward their margins, either the picture is confused by the fragmentation of continents, or belts of mobility can trend across all portions of the globe, irrespective of the boundaries between continents and oceans.

CONCLUSIONS

Igneous and metamorphic mineral dates from all parts of the world tend to occur in the same intervals of cyclic abundance. This suggests that the earth's history is marked by episodes during which the spatial distribution of intense mineralogenic activity shifts, resulting in the selective preservation of "withdrawal dates" for the areas becoming stable.

The spatial distribution of mineral dates in North America defines a sequence of age provinces which are younger nearer the continental margin but does not support the hypothesis of continental accretion. An hypothesis envisioning the gradual outward solidification of an originally mobile continent is more satisfactory but is not supported by the spatial distribution of mineral dates on other continents and does not explain repeated, widespread rejuvenation of stable areas.

Appendix

TABLE OF MINERAL DATE LOCALITIES

It is intended that this list include all localities for which significant igneous and metamorphic mineral dates had appeared by January, 1959. The reader should keep in mind the fact that a large number of these values are at best tentative, and that very few of them are as precise and meaningful as might be wished.

The dates indicated for many localities are composites based upon determinations of several different materials, isotope ratios, or analysts. The criteria used in the selection of significant data, and the means of determining composite ages are treated in the text.

We are not attempting to present a compilation of available age data, but only to list the "locality dates" which we have derived from this data and to give a minimum of information concerning each. For the sake of space this information is compressed into a single line as follows—Locality number. Locality: rock types if known;minerals date:method of age determination used (spread of date determinations considered to be significant) composite date. The sources are indicated by numbers in the extreme righthand column which refer to the list of references cited. A complete bibliography is not given for each locality and original references are not necessarily cited.

Where necessary, ages have been recalculated to accord with constants currently used in North American laboratories (Aldrich, et al., 1956b, Wetherill, 1957).

ABBREVIATIONS USED IN TABLE

Localities		peg	pegmatite
bath	batholith	qtz monz	quartz monzonite
mn	mine	rhy	rhyolite
Rn	Range	sch	schist
Soc	South central	*Minerals*	
twp	township	al, allan	allanite
		b, bio	biotite
Rocks		feld	feldspar
carb	carbonatite	fg	fergusonite
gab	gabbro	lep	lepidolite
gn	gneiss	mon	monazite
gr	granite	m, mus	muscovite
gric	granitic rocks	p, pitch	pitchblende
gro	granodiorite	phlog	phlogopite
hf	hornfels	thor	thorite
mig	migmatite, migmatite gneiss, metasomite	th	thorianite
		sam	samarskite
nsy	nepheline syenite	u, uran	uraninite

Methods

K	potassium 40/argon 40
Rb	rubidium 87/strontium 87
UPb	uranium/lead isotopes, thorium/lead isotopes
UPbc, ThUPbc	chemical uranium, thorium/lead
Pbα	uranium, thorium radiometric/lead spectrographic
rad	radiation damage method
He	helium method
CPb	common lead method
6/7	Pb 206/Pb207
6/8	Pb 206/U238
7/5	Pb 207/U235
8/2	Pb 208/U232

Date suffixes (see text for further explanation)

As	date preferred by source *s* (*s* being last initial of source)
AV	average, generally of two methods
AVs	an average given by the source *s*
H	highest value, usually of two dates by same method
M	date of more satisfactory method or material
R	most recent value
G	average of date cluster
*	not used in the tables due to large discordance
**	not located on index map
***	exception to the rule for averaging different methods
+	beyond age extent of graphs
++	plotted with southeast Asia and Australia
( )	parentheses around a date indicate that it is a *tentative* value (see text for further explanation)

Locality number	Locality: rock; mineral: method	(spread of dates)	composite date	source
NORTH AMERICA				
CANADA				
	Alberta			
1.	Black Creek: granite, biotite; K		(2030)	54
2.	Crowsnest volcanic agglom.: sanidine; K		(98)	88,44
	British Columbia			
3.	Coast Rn batholith: gro: mica,zirc; K,Pbα	(82-114)	105Af	44,87
4.	Sullivan & North Star mines: galena: CPb	(975-1190)	1045AV	22
	Labrador			
5.	Cape Makkovick: pitchblende; 6/7		(~1000) Al	85
6.	Kaipok & Galena L.: galena; CPb	(1685-1740)	(1715) AV	22
7.	Lake Melville: gneiss; ?; K		(1235)	93
8a.	Southwest: gneiss; ? ; K		(1250)	93
8b.	Southwest: gneiss; ? ; K		(1120)	93
8c.	Southwest: gneiss; ? ; K		(1580)	93
	Manitoba			
9.	Flin Flon: gneiss; bio,galena; K,CPb	(1735,1750)	1750M	22,92
10.	Huron claim: peg; u,mon,mus,p,lep; 6/7, Rb	(2470-2650)	2600G	20,21,34,36, 84,98
11.	Winnipeg River; peg; lep,uran; Rb,UPb	(2580-2680)	2600G	10,25,25a,34,36
	New Brunswick			
12.	Fosterville: granite; biotite ?; K		(400)	92
	Newfoundland			
13.	Duffs: granite; feldspar; Rb		(335)	92
14.	St. Lawrence: quartz monzonite: ?; Rb		(910)	92

Locality number	Locality: rock; mineral; method	(spread of dates)	composite date	source
	Northwest Territories			
14a.	Contact Lake: pitchblende; UPb	(1056-1220)	(1100) M	35
15.	Conwayto Lake: pitch; 6/7		(1340)	22
16.	Eldorado, Great Bear Lake: uran,p; UPb	(1330-1480)	1410G	36,49,82
*17.	Yellowknife, Great Bear Lake: gr; mica: K	(1990,2390)		44
18.	Great Slave Lakes: uran, pitch; 6/7	(1700,1850)	1850M	20,21
	Nova Scotia			
19.	Boisdale Hills: bio; Rb	(470,486)	480Af	92
20.	Central: biotite; Rb,K	(365-375)	370G	92
21.	Northern: biotite; Rb	(375-390)	385G	92
22.	Southwest coast: bio,mus,feld; K	(300-340)	325G	92
23.	Southeastern: bio,mus,feld; Rb,K	(345-380)	365G	92
	Ontario			
24.	Bancroft: peg; bio; Rb,K	(850,990)	(920) G	12
25a.	Bathurst Twp: uraninite; 6/7		(1080)	98
25b.	Bathurst Twp: uraninite; 6/7		(1310)	22
25c.	Torry Hill: gr,syenite; zirc,sphene; UPb	(1000-1090)	1000At	8,25a,120
26.	Henvey Twp: uran,feld; 6/7,K	(925,940)	940H	22,107
27.	Blind River: uran; 6/7,K	(1340,1400)	1355AV	92,114
28a.	Brudenell Twp: zirc; UPb		1000AVh	71
28b.	Calabogie: euxenite, sam; 6/7		(1010)	21
28c.	Madawaska: fergusonite; 6/7		(960)	21
29a.	Butt Twp: uraninite; UPb		1020	22
29b.	Cardiff Twp: zirc,u,b,mus,lep; UPb,Rb,K	(960-1030)	1020M	12,21,36
30.	Coldwell: syenite,bio,feld: Rb,K	(947-1053)	1000M	14a
32.	Cutler batholith: mus,feld; Rb	(1700-1760)	1750G	26
	Cutler batholith: bio, Rb,K	(1325,1380)	1355AV	26
34.	Haleyboria: lamprophyre; mica; Rb,K	(2050,2160)	2105AV	26
35.	Hearst: peg,mica; Rb,K	(2540,2600)	2570AV	12
36.	Huntsville: gneiss; ?,K		(1000)	92
37.	Karabake Falls; granite; mica? ; K		(2570)	14a
38.	Levack: norite; mica; Rb		(1830)	26
39.	Long Lac: granite; bio; K		(2320)	93
41a.	Nipissing L., east end; ? ; K		(1380)	92
41b.	South River: gneiss: K		(920)	92
42.	Nipissing L., west end: gneiss; Rb		(970)	92
43.	Round Lake: lamprophyre; mica: Rb,K	(2450,2600)	2595AV	26
44.	Sault Ste. Marie: pitch 6/7	(920-1160)	1100M	20,22
46.	Parry Sound: uran,mica; UPb,K	(990-1030)	994Aw	129,135
47a.	Sudbury, Hart Twp: granite,bio; Rb,K	(1676-1820)	1680Am	93
47b.	Sudbury Cartier Twp: granite; bio; Rb,K	(1600,1623)	1620Am	93
47c.	Sudbury North Range: gabbro,norite; ? ; K,Rb	(1625-1840)	1720AV	92
47d.	Sudbury South Rn: gab,norite,gr,rhy,hf; ? ; Rb,K	(1265-1420)	1390G	92
48.	Timmins: granite, mica; Rb,K	(2470,2520)	2495AV	26
49.	Upsala: gneiss, granite; mica? ; K		(2700)	14a,92
50.	Wavy Lake: granite; mica; Rb,K	(950-1075)	1025AV	26,93

Locality number	Locality: rock; mineral; method	(spread of dates)	composite date	source
	Quebec, also see Vermont			
50a.	Chicoutimi: syenite; hornblende; Rb		(950)	101
51.	Gaspe: pitch, mica ?; 6/7, Rb	(370,375)	375H	22,93
52.	Jeannine Lake, Mt. Reed: peg:mica;K	(1000-1200)	1100AV	56
53.	Mt. Laurier, east of: granite:mica;K		(990)	92
54.	Pied des Monts: uran; UPb	(950-1000)	1000H	22
**55.	Villeneuve: uran; UPb	(880-980)	(965)G	22
	Saskatchewan			
56a.	Beaverlodge:uran, bio;UPb,Rb,K	(1780-1970)	1850M	12,36,129
56b.	Eldorado Mine:primary U minerals;UPb		(1405)	36
56c.	Goldfields: pitchblende; 6/7	(1630-1860)	(1860)H	21,35,81
	Goldfields: pitch (redeposition)6/7	(900-1160)	(~1100)G	36,78,81
57.	Black Lake: pitchblende; 6/7	(1230,1250)	(1250)	21
58.	Charlebois L. :uran,feld:6/7,K	(1780-1800)	1800H,M	21,22
59.	Lac Le Ronge: uraninite; 6/7	(1750,1780)	1750R	21,36
UNITED STATES				
	Alaska			
60.	Birch Creek:granite;zirc;Pbα	(48-56)	(53)AV	94
60a.	Mt.Fairplay:qtz.dior,monzonite;z;Pbα	(93-112)	(103)AV	94
61.	Iditarod quad:quartz monzonite;z;Pbα	(49,60)	(60)H	94
62.	McCarthy quad:granodiorite;zirc;Pbα		(105)	94
63.	Medfra quad:monzonite;zirc;Pbα		(58)	94
64.	Craig C-2 quad;diorite;zirc;Pbα		(103)	94
65.	Taku R. quad:granodiorite;zirc;Pbα		(93)	94
	Arizona			
66.	Bagdad: granite,peg:mus,lep;Rb,K	(1360-1500)	1390G	12
67.	Grand Canyon: gneiss:mica;Rb,K	(1340,1350)	1345AV	12
68.	Wickenburg: muscovite; Rb,K	(1120,1300)	(1210)AV	12
	California			
69.	Death Valley:peg:mus;K,Rb	(1670,1720)	1695	12,130a
70.	Klamath Mtns:tonalite;zirc;Pb	(81,112)	(97)AV	87
71.	Mountain Pass:carb;mon;ThPb,UTh, Pbc,Pbα	(849-955)	(950)G	74
72a.	Pala: pegmatite; lepidolite; Rb,K	(89-119)	106G	10,42,54,132
72b.	Peninsula Range bath:granitic;zirc;Pbα	(75-136)	110Al	71,87
73.	San Gabriel Mtns: gabbro;zirc		(930)H	42
74.	Sierra Nevada,Bishop:granitic;zirc;Pbα	(90-111)	102Al	87
75.	Sierra Nevada,Yosemite:gric;peg; mica;K	(76.9-95.3)	90G	39,71,87
**75a.	Sutter Buttes:rhy,andesite;bio;K	(1.57,1.69)	1.69H	23
76.	Transverse Ranges:?;K?		(100)	12
	Colorado			
77.	Gunnison Co.:peg,lep,mus,zirc;Rb,K, UPb	(980-1020)	995AV	4,6,8,9,17
78.	Front Range:uran;6/8,7/5	(55-70)	60G	15,16,37,98, 100,112,113
79.	Mesa County: granite;bio;Rb,K	(1300-1370)	1330AV	12
	Mesa County: granite;xenotime;6/7	(1650-1810)	1700G	6,7,118,136
80.	Pikes Peak:granite;bio,zirc;K,Rb,UPb	(980-1020)	995AV	12

Locality number	Locality: rock; mineral; method	(spread of dates)	composite date	source
	Connecticut			
81.	Branchville:peg;uran,mus;UPb,K	(367-382)	370G	130,135
82.	Soc: peg,sch,gn;mus,lep,bio,sam;UPb,K	(230-292)	265Ae	36,93,98,106, 130
	District of Columbia, see Washington, D. C.			
	Georgia			
83.	Eastern piedmont:gr,gn;bio,mus;Rb,K	(250-360)	288G	83
	Eastern piedmont:granite;gn;zirc;UPb	(450-490)	485G	57b
	Idaho			
84.	Coeur'd Alene:uran,zirc,xeno,mon;6/7	(850-1035)	(1035) R	36,78
85.	Idaho batholith;granitic;zirc;Pbα,rad	(88-130)	108Al	61a,71,87
	Maine			
86.	Calais:biotite; Rb		(515)	61
87.	East coast:granitic;feld;K	(325-373)	(335) G	93
88.	Northern:granitic;gn;bio?;K	(340-397)	(370) G	93
89.	Northwestern;granite,gn;bio?;K	(293-294)	(294) G	93
90.	South coastal;granite,sch;K	(247-295)	(250) G	93
	Maryland - Pennsylvania			
91a.	Central Maryland:gn,sch;bio;Rb,K	(305-320)	310Ad	28,122
91b.	Phila.-Baltimore:gn;z,microcline;Rb,K, UPb	(1050-1120)	1050At	12,28,122
	Massachusetts			
93.	Eastern:granite;bio,zirc;K,Rb,Pbα	(310-385)	325G	40,93,131
	Eastern:granite;bio,zirc;K,Rb,Pbα	(215-270)	245G	40,93,131
	Michigan			
94.	Iron,Dickinson Cos:peg,gn;bio,mus;Rb, K	(1620-1830)	1760G	5
	Iron,Dickinson:granite,gn;bio,mus;K,Rb	(1240-1420)	1400G	5
	Minnesota			
95.	Duluth, Beaver Bay:gabbro;mica;K	(1100,1100)	1100	55
96.	Ely:granite;biotite; K		(2380)	54
97.	International Falls:granite,bio;Rb,K	(2610,2630)	2620AV	27
98.	Montevideo:gneiss;bio;K	(1820-1870)	1845AV	16
99.	Morton:gneiss;biotite; K	(2550-2650)	2620AV	16,54
100.	NW Angle, Vermilion Rn.:peg;mus;K	(2500-2700)	2600AV	46,55
101.	Ontario boundary:gneiss;mica;K		(2700)	55
102.	Pierz:biotite; K		(1580)	54
103.	Rockville:granite;bio;Rb,K	(1650,1690)	1690H	54,72
104.	Sacred Heart:granite,peg;bio;K,Rb	(2320-2530)	2515G	16,72
105.	St. Cloud:biotite; K,Rb	(1775-1870)	1855H-AV	54,72
106.	Snowbank Lake: biotite; K		(1230)	54
107.	Thompson fm.: schist;mica;K	(1640-1730)	1720G	54
	Missouri			
108.	Fredericktown: mus;Rb,K, CPb	(1405-1450)	1425AV	27,142
109.	Decaturville: peg,mus; Rb		(1450)	27

Locality number	Locality: rock; mineral; method	dates) (spread of	composite date	source
	Montana			
110.	Bearpaw uplift			
111.	Beartooth Mtns.:mica:K,Rb	(2520-2700)	2610AV	45
112.	Boulder bath.:gric;zirc,mon,feld:Pbα,K	(61-72)	71G	18,19,79
113.	Cook City: peg,uran;UPb	(2600-2700)	2690HG	49
	New Hampshire			
114.	Oliverian magma ser.:gric;mus;K,Pbα	(288-340)	340M	24,89
115.	Conway:granitic;bio,mus,zirc;K,Rb,UPb	(168-195)	178AV	12,72,93,120
116.	Mt. Monadnock:schist;bio:Rb		(490)	123
117.	Northern:phyllite,sch,gro:K	(322-340)	335G	93
118.	Ruggles mine:uraninite; 6/7		(455)	21
	New Jersey			
119.	Hiberia:gneiss;bio,Rb,K	(790,920)	(920) H***	27
	New Mexico			
120.	Sandia Mtn.:granite;mica;Rb,K	(1300-1340)	1320AV	12
121.	Harding mine:peg;mus,lep;Rb,K	(1250-1350)	1300G	12
	Harding mine:peg;microlite;UPb	(940-970)	~960M	12
122.	Las Vegas: monazite; 6/7		(1340)	98
123.	Mora County: mica; Rb,K	(1280,1490)	(1385) AV	12
124.	Petaka: zirc, mon, xeno; 6/7		(875)	35
	New York			
125.	Bedford:peg;cyrtolite,uran; UPb	(300-420)	350Ac	36,97,106
126.	Canada Hill, Bear Mtn:zirc,bio;UPb,Rb	(930-1170)	1040G	26,27
127.	Natural Bridge:syenite contact;zirc;6/7		(1140)	120
	North Carolina			
128.	Bryson City: mica, K	(560,580)	580H	
129.	Spruce Pine:peg;uran,sam,mus;UPb,K, Rb	(335-420)	370Ad	12,17,21,86, 134,135
	Spruce Pine:gneiss; zirc; 6/7		(1270)	27
131.	Western, E. Tenn.:mica; K		(~1000)	17
	Oklahoma			
132a.	Arbuckle Mtns.:zirc; Pbα	(900-980)	(940) AVh	58
132b.	Troy; biotite; Rb		(1360)	27
133.	Wichita Mtns:peg;zirc,bio;UPb,Rb,K	(460-550)	550M	12
	Oregon			
134.	Baker County: granitic; zirc; Pbα		(102)	87
	Pennsylvania, See Maryland			
	South Dakota			
135.	Keystone:peg;lep,mus;UPb,Rb,K	(1550-1730)	1650Ad	12,27
136.	Milbank: granite, bio, K		(2070)	54
	Tennessee, See North Carolina			
	Texas			
137.	Llano Co.:granite;zirc,mica;UPb,K,Rb	(1060-1100)	1070M	12,26
	Utah			
**138.	Happy Jack mine:uran; 6/8, 7/5	(65,65)	65	112

Locality number	Locality: rock; mineral; method	(spread of dates)	composite date	source
	Vermont			
139.	Northern, & adjacent Quebec: ? ; Rb,K	(330-346)	340G	93
	Virginia			
140.	Mary's Rock: gneiss; zirc,bio;UPb,Rb,K	(800-1150)	1100G	27,122
	Washington, D. C.			
141.	Kensington gneiss: zirc,bio;6/7,Rb,K	(305-550)	530M	27
	Washington			
142.	Coast Range bath.:granitic;zirc;Pbα	(87-134)	105Al	87
	Wisconsin			
143.	Marmette Co.:granite;bio;K,Rb	(1230-1370)	1300AV	5
144.	Mellen: granite; bio, feld; K	(1005,1100)	(1005M)	54
145.	Waupaca: granite, bio; K		(1480)	54
	Wyoming			
146.	Bighorn Mtn.:granite, gn; K,Rb	(2540,2760)	2690AV	45
147.	Bonneville: peg; lep, mus; Rb,K	(2250-2470)	2415AV	12,25a
148.	Sherman; granite; bio; K,Rb	(1300,1410)	1395AV	27
149.	Shoshone Gorge: bio; Rb		(2720)	45
150.	Southcentral: ?		(1650)	27
151.	Southwestern: ?		(1650)	27
MEXICO				
152.	Baja Calif.:gric.; zirc, mon;UPb, Pbα	(98-115)	115M	87,110
153.	Guerrero; granitic; zirc; Pbα	(96-101)	101H	87
154.	Oaxaca; granitic; zirc; Pbα	(96,108)	(108)H	87
SOUTH AMERICA				
	BRAZIL			
	Bacoa quad.: granodiorite; bio; K	(2440,2510)	2510H	93
	Bahia, Itambé: mon, samarskite; UPbc	(361-380)	375G	91
	Cachoeira do Campo: mig gneiss; bio, K	(720,760)	760H	93
	Dom Bosco: gneiss; ?; K		(530)	93
	Itabira quad.: gneiss; bio, mus; K	(450-500)	460G	93
	Itabirito & Belo Hor. quads: mig; bio;K	(1340,1360)	1360H	93
	Ibirtite: granite; ?; K		(550)	93
	Minas Gerais: mon; UPbc	(942-993)	(990)G	91
	Peti Reservoir: granite; bio; K		(460)	93
	Rio de Janeiro: gneiss; bio; K		(490)	54
	COLOMBIA			
	Guayana shield, west edge: bio; K		(484)	93
EUROPE AND NORTHERN ASIA				
	CZECHOSLOVAKIA			
	Jachymov: pitchblende; UPb		179	85
	Razna Twp.; Moravia: lepidolite, Rb		(410)	77
	FINLAND			
	Koirala Nouskio: biotite, K		(1790)	115
	Koli: gneiss; zirc; 6/7		(2650)	27
	Koli: gneiss; bio; Rb,K		1800Ad	27

Locality: rock; mineral; method	(spread of dates)	composite date	source
FRANCE			
Andlau, Vosges Mtn.:gr.; zirc; Pbα	(215-250)	(235) AV	59
Natzwiller Vosges Mtn.: gr; zirc; Pbα	(293-320)	(305) AV	59
St. Sylvestre, Limoges: pitch; UPb		(150)	30
GERMANY			
Dresden, E. Lausitz:gro:zirc,bio;UPb,K	(367-408)	400G	109
Hechtsberg: bio, feld; K	(237-255)	255M	47
Mansfeld: pitch, 6/7		(395)	37
NORWAY			
Arendal district: peg, microcline; K		(1020)	14
Aust-Agder, Telemark: cleveite; UPb		1090	97
Brevik, Telemark: Thorite; 6/7		(355)	97
Hobol: mus. orthoclase; K	(895-965)	965M	47
Kalstad: euxenite: 6/7, 8/2		960	84
Oslo area: syenite; mica; K		(985)	14a
Romteland: uran, eux, thorite; UPb		920H	84
Tvedestrand, Telemark: thorite; 6/7		(610)	37
SCOTLAND			
Outer Hebrides: peg, microcline, K	(880-1140)	(1060) Ah	69
SWEDEN			
Grave: euxenite; UPbc		(675)	99
Stackebo & Nol: uran, nolelite; UPbc	(900,960)	(960) H	99
Stockholm neigh.:peg; u, fg, hjilmite; UPbc		(1770)	99
Stockholm neigh: mon; UPbc		(1375)	99
Varuträsk: lepidolite; Rb	(1720,1760)	1740AV	12
Vaddo: yttrotantalite; UPbc		(575)	99
SPAIN			
Sierra Albarrana, Cordova: mus, u; Rb, UPb		280	29
U.S.S.R.			
Asiatic			
Aldan, Siberia: biotite, K		(110)	48a
Aldansky shield, Siberia: vein; phlog; K	(1860-1940)	1925G	103
Altai: lep, serizitolite; K, He	(240,245)	240M	48a
BaikalL.,Sib.:mon,al,z,thor,phlog;6/7	(450-500)	480G	103
Buryat Mongolia: mus; K		(270)	48a
Cape Tiganoss, Siberia: peg; mus;K		(1765)	103
Coastal Siberia: granitic;?;K	(75-100)	90G	102
Eliseevka: peg: broggerite,mus; 6/7, K	(2035,2130)	2080AV	111
Kenady River, Siberia:gneiss; bio;K		(1970)	103
Mamsky region, Siberia: mica:K,Rb	(350,420)	385AV	111
North Tian Shan: granite; ?;	(320-345)	(335) AVs	111
North Tian Shan: granite; ?;	(240-270)	(255) AVs	111
Sikhote-Alin Mtns: granitic:?; K	(50-75)	65G	102
South Primoria: granitic;?; K	(135-155)	(150)	102
Tallus Altai, Komyshtag: granite;bio;K		(345)	102
Turkestanski, Cherbet Mtns: mus; K		(225)	48a
Voznesenka: granite; mus; K	(345,345)	345	102
Zahaykalije: peg: mus, microcline; K	(135,140)	140M	102

Locality: rock; mineral; method	(spread of dates)	composite date	source
Caucasus			
Balksan R.:granite; bio; K		(365)	117
Balksan R.: granite; bio; K		(105)	117
Caucasus: muscovite; K		(340)	48a
Galiat, N. Osetia: granite; bio; K		(215)	117
Kassar R. gorge: granite; bio; K		(230)	117
Kubany R. headwaters:granite; bio; K	(285,285)	285	117
Malka R. headwaters: granite; bio; K		(240)	117
Main Rn. complex: granite; bio; K		(465)	117
Main Rn. Cherek Bezengski granite:bio;K		(280)	117
Northern complex: granite; mus; K		(375)	117
Sanguti Don glacier: granodiorite;bio;K		(145)	117
Tepli: granodiorite; bio; K		(90)	117
Tyrny Aus: granite; bio; K	(83-115)	100AV	117
Tyrny Aus: leparite; bio; K		(15)	117
Zey R. valley: granite; bio; K		(130)	117
Karelia, Kola Peninsula, White Sea Area			
Alakurtti: monazite; UPb	(1920-2200)	2100G	143
Belomorye: peg; mus, bio; K, He	(1720-1850)	1800G	48a
Black Salma: uraninite; 6/7		(1740)	48
Cape Kartash: biotite; K	(1880-1900)	1900H	48
Cape Kindo: biotite; K		(1785)	48
Chkalov mine: uraninite; 6/7		(1760)	48
Chkalov mine: monazite; 6/7		(1930)	48
Demenikha Is.: granite; mica; K		(1960)	103
Eighth of March vein:peg,contact;m,b;K	(1775-1825)	1805G	48
Giblova Luda: biotite; K	(1805,1860)	1860H	48
Gimolekoe L.: schist; mus; K		(1785)	48
Guimaly: schist; bio; K		(1805)	48
Kamennaja Taibola: uran; 6/7		(1800)	48
Karelia, east central:granite:bio;K	(1565-1585)	1580G	48a
Karelia vein #1: mig, gneiss; bio; K		(1900)	48
Keyvy: peg, schist; mus; K	(1590-1735)	1640G	48
Khisovara: schist; bio; K		(1700)	48
Koita Tundra:allan,cyrtolite,uran;UPb	(1700-1810)	1820Az	144
Kontozero: gneiss, granite; mica; K?	(2250-2390)	2310G	103
Kontozero: granite; bio; K		(1150)	48
Kopatvaraka: gneiss; mica; K		(1920)	103
Lesovataja Luda: bio; K		(1740)	48
Malinovajaraka: mus; K?		(1880)	48
Medvedka: sphene: UPb	(1650-1800)	1800H	144
Mramovnyi Is.: gneiss;bio,mus; K?		(1795)	48
Niva Jarvi L.:mylonite; bio; K		(2065)	48
NE Baltic shield: biotite; K		(1785)	48a
North Ladoga:sch,granite;bio,mus;K	(1680,1720)	1720H	48
Ohljabinin Is.: biotite; K		(1735)	48
Panphylova Varaka: bio; K?		(1870)	48
Parandovo: schist; bio; K		(1730)	48
Pertivaraka: peg contact;bio;mus;K	(1815,1880)	1880H	48

Locality: rock; mineral; method	(spread of dates)	composite date	source
Pjuhja Jarvi L.: schist, mus; K		(1720)	48
Ponygom: granite; bio; K		(1845)	48
Priladogie:sch,peg;bio,mus,quartz:K	(1710-1775)	1765G	48,48a
Sludovaraka: mus; K		(1855)	48
Sopka Besymjannaja: peg: mus; K		(1795)	48
Suprotivnji: biotite; K		(1710)	48
Tedino L.:allan,mon,carboron:UPb	(1830-1860)	1860H	143
Tichka R.: peg; mus; K		(1845)	48
Trjasova Luda: vein:mus,bio,K	(1765,1785)	1785H	48
Tundra Ohmylk: granite: mus; K		(0825)	48
Tundra Ohmylk: peg: mus; K		(2055)	48
Uljalega: schist; bio; K	(1600,1620)	1620H	48
Uljalega: peg: mus; K	(2345,2470)	2470H	48
Uvv-Uaya:granite,peg: mus; K	(1785-1825)	1825H	48
Valetov Island: mus; K	(1695,1750)	1750H	48
Vichennaja Luda: gneiss:bio:K	(1785-1935)	1800G	48
Vichennaja Luda: mig:gneiss:bio:K	(2075-2315)	2305G	48
Viiborg massif:rapakivi gr;bio,feld;K	(1420-1575)	1510G	48
Vincha R.:schist: mus; K		(1690)	48
Voronya R.:gneiss,granite: mica; Rb	(2600,2650)	2650H	103
Vorony Tundra:peg;green mus; K?		(2140)	48
Vuori-Jarvi L.: phlogopite; K	(370,380)	380H	48
Ukraine			
Chlebodarorka, Azov:alkali massif;z;6/7		(2080)	127
Chudnovo-Berdischev complex:mon;UPb	(2125-2250)	2100	80
Dneprovsko-Tokobsknj:aplite;bio,mon; 6/7, K	(2000,2050)	2025AV	127
Gitomir: peg, mus; K		(1910)	103
Korostichev: peg, mus; K		(1880)	103
Kirovograd complex:granite,peg:mica:K	(1870-1885)	1880G	102
Korosten complex:rapakivi gr; mica: UPb,K	(1700-1750)	1725G	103
Korostjenskyi: peg; mus,feld; K	(1715-1765)	1765M	48
Korsuny, Azov Sea:gr;zirc,al,bio;UPb,K	(1750-1760)	1760G	127
Krivog Rog:mig;malacon,hydrobio;6/7, K	(1730-1865)	1820AV	127
Krivorogye: schist; mica; K	(1890-1930)	1930H	103
Liporez: Sobits fm; mon; UPb	(2030-2180)	2100G	80
Malin, Azov Sea: zircon; 6/7		(1700)	127
Mogilev: charnokits fm;mon;UPb	(1975-2155)	2155H	80
Mariupole complex:peg,syenite;b,feld;K	(1485,1525)	1485M	48
Petrovo:peg,geniss; mica; K	(2060,2060)	2060	103
St. Andreevka,Azov Sea:peg;mus;K		(1950)	48
Saksagany:migmatite;allanite;UPb	(2420-2780)	2630AV	127
Saksagany:granite,gn,nsy;bio;K	(2030-2295)	2190G	48,102
Shevchenko-Bakojak massif:gr;bio;K		(1870)	48
Shpola,Azov Sea:rapakivi gr;zirc;UPb	(1700-1750)	1750H	127
Spanov,Salychia,Visla:nsy;z,al,mon,b; 6/7, K	(1640-1920)	1850G	127
Teterev R.:marble;bio;K		(1960)	48

Locality: rock; mineral; method	(spread of dates)	composite date	source
Umansko-Novo-Mirgorod:granite:bio;K	(1450-1645)	1600G	127
Zelenaja Mogila:peg,mus;K		(2005)	48
Zitomir complex: mon, zirc, mus, bio; UPb, K	(1705-1925)	1820M	48,127
AFRICA			
BELGIAN CONGO			
Boma;lower Congo:biotite;K	(446-496)	470G	70
Manono:lipidolite;K,Rb	(840-975)	910AV	12
Mitwaba,N.K.:yttro,lep,galena;UPb,CPb	(920-1110)	1040M	70
Muika:lepidolite;K,Rb	(915-950)	935AV	12
Shinkolobwe,S. Katanga:pitch;UPb		610Ah	70
EGYPT (U.A.R.)			
Eastern desert:biotite;K	(600,600)	600	93
FRENCH WEST AFRICA			
Ivory Coast:u,z,galena;UPb,Pbα,CPb	(1950-2310)	2180G	33,70
GHANA			
East of Konongo:peg;feld;K		(1645)	70
KENYA			
Nairobi area: peg;feld;K	(410-470)	(465)G	70
Tura:peg;sam,feld;UPb,K	(450-485)	485Ah	70
MADAGASCAR			
Antisirabe:alluvial mon; UPb	(2420-2790)	2680AV	1,2,3,70,96
Bemasoandro:peg,uran;UPb	(395-490)	490Ah	66,70
Betroka:peg;thorianite;UPb	(480-510)	490Ah	42,66,70
Manangotry Pass: mon;6/7		(1140) Ah	70
Sahatany Valley:peg;lep;Rb	(550,560)	560H	95
Soafia:peg;thorianite;UPb	(450-500)	480Ah	66
Tsarafara:lepidolite;Rb		(652)	75
Voandolaka: euxenite; 6/7	(620,645)	645H	70,139
MOROCCO			
Central Altai: mica; K		1650AVh	70
MOZAMBIQUE			
Alto Ligonha:peg;sam,lep;Rb,UPbc	(435-480)	460M	70,95
Ribaué: samarskite; 6/7		(650) Ah	70
Uluguru Range: pitch; 6/7		(620)	42
NIGERIA			
Dogon Dagi: peg; lep; Rb	(475,510)	475R	95,109
Rayfield: placer mon; 6/7		(485) Ah	70
NORTHERN RHODESIA			
Irumi Hills: uran, mon; UPb	(2560-2780)	2560Ah	1,2,70,96
Lundazi: peg; betafite; UPb	(435-485)	485Ah	70
Nkana: uraninite; UPb	(527-612)	(612) Ah	70
NYASALAND			
Tambane dist:nsy gneiss;zirc;Pbα	(515-609)	(550) G	70,42

Locality: rock; mineral; method	(spread of dates)	composite date	source
SIERRA LEONE			
Sula Mtns.: alluvial mon, galena: UPb, CPb	(2930,2940)	2940 Ah	24,70,139
SOUTHERN RHODESIA			
Beitbridge: U minerals, titanite: UPb	(1935-2120)	2080G	61,130
Bikita quarry: mon.mica,lep; UPb,Rb,K	(2640-2700)	2680G	12
Forfar farm: peg, lep; Rb		(2490)	70
Jack tin claims: mon; 6/7	(2640-2650)	2640 Ah	3,70
Pope tantalum mine: mon,lep; UPb,Rb,K	(2410-2810)	~2510 Ah	70,139
Urunque, Miami: betafite; UPb	(400-445)	440 Ah	70
SOUTHWEST AFRICA			
Karibib district: lepidolite; Rb	(475-550)	545G	70
Kinderzitt: lepidolite; Rb	(820,990)	990H	70
RUANDA-URUNDI			
Runinya: monazite; 6/7		(2190) Ah	70
SWAZILAND			
Kelly mine: yttrotantalite; 6/7		(2060)	70,84
TANGANYIKA			
Hombolo, Chenene Hills: lepidolite; Rb	(2440-2640)	2600G	70,95,132
Karema: muscovite; K, Rb	(950,1100)	1025 AV	11
Morogoro: uraninite; UPb	(595-620)	610G	37,70
UGANDA			
Kampala Buganda: lepidolite; Rb	(1845-1870)	1850R	70
Nanseke, Toro: quartz vein; euxenite; 6/7		(1370)	70
UNION OF SOUTH AFRICA			
Basal-Vaal-Bird reef: uran; 6/7		(2130) Ah	70
Capetown: gr; bio,zirc; 6/7,Rb	(505-670)	575 At	5,70,132
Contact reef, Ventersdorp: uran; 6/7		(2210) Ah	70
Dominion Reef: uraninite; UPb	(2680-2930)	2760 Ah s	3,70
Goodhouse, Cape Province: peg; mon,u; UPb	(850-945)	900 At	70,121
Gordonia, Cape Province: peg,u: UPb	(965-1040)	1035 Ah	70
Houtenbeck, Bushvelt: felsite; mon; 6/7	(900,935)	935 At	119,121
Kruger Natl. Pk.: lithium mica; Rb		(960)	70
+ Letaba, Transvaal: lep; Rb		(3075)	70,95
Loolekop, E. Transvaal: th,uranof; UPb	(2000-2060)	2060H	70
Marievale: uraninite; UPb	(2130-2220)	2130 Ah	70
Mica Siding, NE transvaal; Lep; Rb		(2040)	75
Jakalswater, Namaqualand: mus,lep; K, Rb	(920-965)	950G	11,70
Nigel mine Main Reef: uran; UPb	(1990-2260)	2110 AV	70
Steenkampskraal, C.P.: qtz vein; mon; UPb	(990-1170)	1035 AVt	121
SOUTHERN ASIA AND AUSTRALIA			
INDIA AND PAKISTAN			
Ankapalle, E. Ghats: allanite; UPbc		(1585)	90
Nellore, E. Ghats: peg; sam; UPbc	(1550-1765)	1760G	13,69,90

Locality: rock; mineral; method	(spread of dates)	composite date	source
Pichchli, Bihar: mon; UPbc		(970)	13
Rajputana: peg: uran; UPb	(735-740)	735Ah	65,69
Ranchi, Bihar: allanite; UPbc	(980,980)	(980)	13
Singar, Bihar: peg, mon, allanite; UPb	(885-1005)	995H	65,69
Soniana: peg: mon; UPb		1016An	96,121
Yaduir, Mysore: mon; UPb		2605An	96
CEYLON			
Alluvium: zircon; UPb	(538-555)	550At	118
Balangoda: thorianite; UPb	(461-531)	(530)H	69,97
INDONESIA			
Billiton: biotite; K		(180)	93a
Singkep, Sumatra: granite; mon; 6/8, 8/2	(140,160)	160H	109
++*JAPAN*			
Iisaka:peg;u;UPbc checked isotopically		(105)	87
AUSTRALIA			
Catlin Creek: peg; mus, microcline; K, Rb	(2770,2800)	2785AV	8,76
Katherine-Darwin, N.T.:bio, mus; K	(1560-1720)	1695G	93
+Kubuta: peg; lep; Rb		(3200)	25a
Londonderry & Grossmont:peg;mus,lep; K,Rb	(2660-2775)	2705AV	93(p. 94)
Mt. Isa Mine, Queensland:mon;6/7,8/2	(1000,1160)	1080AV	121
Nichol's Nob: uran: UPb	(430-445)	440G	84
N. Territory, north central:bio,mus;K	(1320-1540)	1480G	93
N. Territory, south central; bio; K	(1420-1510)	1460G	93
Radium Hill: davidite; 6/7		(1540)	21
Western Australia: xenotime; UPbc		(450)	57,69
++*ANTARCTICA*			
McMurdo Sound: gneiss, biotite; K		(520)	56a

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RELATIONSHIPS BETWEEN LENGTH OF ARC AND THICKNESS OF PTYGMATICALLY FOLDED VEINS

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ABSTRACT. Certain aspects of folding of a competent rock layer (ptygmatic vein) embedded in incompetent rocks is treated theoretically. If both rocks are considered as Newtonian substances with high viscosity coefficients, one finds the following relationship between initial wavelength, λ_i, (= length of arc of a wave), thickness of competent layer, $2h$, and viscosity coefficient of competent and incompetent rocks, μ_1 and μ_2, respectively:

$$\lambda_i = 2\pi h \sqrt[3]{\frac{2}{3}\mu_1/\mu_2}$$

The buckling layer gives rise to a sinusoidal contact strain in the host. The depth of penetration of the contact strain into the host is calculated to be $Z_c = \frac{2}{\pi}\lambda_i$. This agrees well with experiments.

INTRODUCTION

The reasons for the sinusoidal shape of ptygmatic veins in gneisses and schists have been subject to considerable discussion with several dynamic models suggested by, for example, Sederholm (1913), Wilson (1952), Godfrey (1954), Kuenen (1938) and Ramberg (1952, 1956 and 1959). Field studies and experiments have made the present author believe that the undulatory shape of such bodies is generally caused by compressive plastic strain in the host rock along directions parallel to the vein which responds to the shortening by folding rather than simple compression. The reason that the vein responds by folding whereas the adjacent host rock responds by plastic compressive strain is a difference in competency of the two rock types, the vein being more competent than the host.

Experimental and theoretical studies of ptygmatic folding have been reported in an earlier paper by the author (1959). Subsequent considerations, however, have resulted in a more exact mathematical expression for length of arc of folds and thickness of vein as related to difference in viscosity (competency) of vein and host rock. This relationship is developed in the present article together with an expression for the "depth of contact-strain penetration". The latter refers to the fact that the transversal movement of the folds along the vein creates sinusoidal strain in the adjacent rock, this contact strain gradually diminishing to zero at a certain distance from the folded vein.

In order to develop these relations we shall assume both vein and host rock to behave mechanically as Newtonian substances, i.e., rate of strain is proportional to stress and their yield point is zero. This seems a reasonable assumption for the slow deformation or microcreep which occurs in crystalline rocks under the relatively high P,T conditions at which ptymagtic folding generally forms. Imagine furthermore the vein as an evenly thick plate of finite length and width enclosed in an infinite body (or very large as compared with the vein) of homogeneous rock, the vein being more viscous than the host

rock. The host rock with its enclosed vein is affected by stresses which create homogeneous strain throughout the body. Let the vein be oriented parallel to the principal longitudinal compressive strain in the host rock. The compressive strain in the rock adjacent to the vein will induce compressive stress in the vein as a result of skin friction. The vein may consequently start to buckle if the induced stress is strong enough and if it is maintained over a sufficient length of time.

Now in order to find the wave length of the initial folds at the moment they start to form we shall first determine the resistive force which the vein itself would offer against buckling if it was not surrounded by a substance with some strength or viscosity. The resistance against buckling offered by the vein itself decreases with increasing wave length in a similar fashion as the well known buckling strength of elastic plates. Then we shall consider the resistance which the viscous host rock offers against the development of the contact sinusoidal strain adjacent to the folded vein. This resistive force increases with increasing wave length of the ptygmatic vein. The sum of these two resistive forces is the total force which acts against the evolution of folds along the vein. It will be shown that the total resistance force has a minimum value at a certain initial wave length depending upon thickness of vein and viscosity of vein and host. The actually developed folds assume initial wave lengths corresponding to the minimum resistive force.

It is felt that the reader may appreciate the theoretical considerations in this article if one of the experimental results from the author's earlier work is reproduced (fig. 4).

BUCKLING OF A VISCOUS PLATE NOT RESTRAINED BY ENCLOSING SUBSTANCE

Whereas elastic buckling of solid plates is a topic of discussion in elementary text books in the field of mechanical engineering, the buckling of plastic plates is much less studied. When it comes to substances of the kind considered here, viz. Newtonian substances with very high viscosity but zero yield point, the author is not aware of any published discussion. It seems therefore necessary to develop a theory of viscose buckling of plates on basis of elementary principles.

Consider an evenly thick plate of thickness $2h_o$ exposed to a compressive stress σ_x in direction x in the plane of the plate. Let the principle stresses σ_y

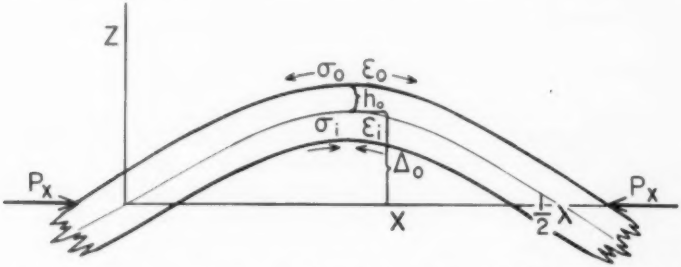

Fig. 1. Crossection perpendicular to fold axis (y) of sinusoidal buckle in a solid plate.

and σ_z be zero. Assume that the surrouding substance does not in any way resist the development of buckles in the plate (the effect of the surroundings is treated separately below).

When a small-amplitude buckle develops, the concave surface of the buckle is affected by compressive strain and the convex surface by tensile strain in direction perpendicular to the fold axes y and parallel to the surface. These longitudinal strains assume maximum values at the outer surfaces and vary linearly with distance from the neutral middle surface where the strain vanishes (fig. 1).

The strains are related to radius of curvature R and distance h from the neutral middle surface:

(1) $\varepsilon_h \cong h/R$ which is valid for small-amplitude buckles (see for example Prescott, 1946); h is reckoned negative on the concave- and positive on the convex side of the neutral middle surface.

Assuming that the buckle is sinusoidal:

$$\Delta = \Delta_0 \sin \frac{2\pi x}{\lambda} \tag{2}$$

and using the conventional formula for radius of curvature, $R = \dfrac{\left(1+\left(\dfrac{\partial\Delta}{\partial x}\right)^2\right)^{3/2}}{\dfrac{\partial^2\Delta}{\partial x^2}}$, gives:

$$|R| = \left|\frac{\lambda^2}{4\pi^2\Delta_0}\right| \quad \text{at } x = \lambda/4 \tag{3}$$

where the radius of curvature is at minimum and the strain at maximum values. Δ is deflection of the neutral middle surface at x, and Δ_0 is amplitude of the fold.

Equation (3) in (1) gives:

$$\varepsilon_h = \frac{4\Delta_0\pi^2 h}{\lambda^2} \tag{4}$$

As the plate is assumed to behave as a Newtonian substance the stresses which correspond to the strains are proportional to the rate of change of strain:

$$\sigma_h = 4\mu_1 \, \partial\varepsilon_h/\partial t \tag{5}$$

where μ_1 is the viscosity coefficient of the plate and the factor 4 arises from the fact that the strain is essentially two dimensional in the x,y plane with practically zero strain parallel to z (see Jaeger, 1956, p. 71).

The stress σ_h is related to the thrust P_x acting on the edges of the plate and the amplitude of the buckle because bending moment, $P_x\Delta_0$, per unit length in y, is balanced by the moment of the stresses in the apex of the buckle:

$$(6) \qquad P_x\Delta_o = \int_{-h}^{h} \frac{\sigma_{h_o}}{h_o} h^2 \partial h = \frac{2}{3}\sigma_{h_o} h^2_o = \frac{8}{3}\mu_1 \, h^2_o \, \partial\varepsilon_{h_o}/\partial t$$

where σ_{h_o} and ε_{h_o} are stress and strain across the axial plane at the outer surfaces of the buckled plate.

It will become clear below that we need to know P_x as a function of the rate of relative shortening of the folded plate in the x dimension, i.e., as a function of $\frac{\partial\lambda}{\lambda}$, at *constant length of arc of the fold*. Now the relation between $\partial\varepsilon_{h_o}$ and $\frac{\partial\lambda}{\lambda}$ at constant length of arc during the folding is readily developed on basis of the expression for length of arc of sinusoidal folds with very small amplitude/wave length ratio:

$$(7) \qquad \lambda_i^2 = \lambda^2 + 2\pi^2\Delta^2_o$$

where λ_i is length of arc which is identical to the initial wave length at the moment the fold starts to develop. The term $2\pi^2\Delta^2_o$ is negligible relative to λ, hence λ in eq. (4) can be replaced by λ_i, and differentiation with respect to Δ_o gives:

$$(8) \qquad \partial\varepsilon_{h_o} = \frac{4\pi^2 h_o}{\lambda_i^2}\partial\Delta_o$$

This equation shows how the strain in the apex of the buckle varies with amplitude when the length of arc remains constant and Δ_o/λ is very small. We are however seeking the relation between $\partial\varepsilon_{ho}$ and $\partial\lambda$ at constant length of arc. Differentiation of equation (7) at constant λ_i gives:

$$(9) \qquad \partial\Delta_o = -\frac{\lambda}{2\pi^2\Delta_o}\partial\lambda,$$

consequently:

$$(10) \qquad \partial\varepsilon_{h_o} = -\frac{2h_o\lambda}{\Delta_o\lambda_i^2}\partial\lambda,$$

which inserted in equation (6) gives:

$$(11) \qquad P_x = -\frac{16\mu_1 h^3\lambda\partial\lambda}{3\Delta_o^2\lambda_i^2\partial t}.$$

Substituting for Δ_o by equation (7) results in the following expression for the thrust P_x needed to make the viscose plate buckle at a rate $\frac{\lambda\partial t}{\partial\lambda}$ provided that the shortening, $\frac{\lambda-\lambda_i}{\lambda_i}$, is very small:

$$(12) \qquad P_x = -\frac{32\pi^2\mu_1 h_o^3\partial\lambda}{3(\lambda^2_1-\lambda^2)\lambda\partial t}$$

This equation refers to a small-amplitude viscose buckling of a plate of thickness $2h_0$ affected by a compressive force $P_x \cdot a$ on two opposite edges of length a. The other edges are free, and the surrounding material does not offer resistance against the buckling. The length of the folds along the fold axes (y) is assumed to be considerably greater than the wave length, otherwise a cross-folding with x as axes will develop (because of longitudinal laminar flow parallel to y in the buckles).

Incidentally, if we introduce relative shortening $\varepsilon_x = \dfrac{\lambda - \lambda_i}{\lambda_i}$ in equation (12), thus:

$$P_x = \frac{16\,\pi^2 \mu_1\, h_0^3\, \partial \varepsilon_x}{3\,\lambda_1^2\, \varepsilon_x\, \partial t}, \tag{13}$$

we see that it is similar to the Euler's equation for initial buckling of elastic plates under a thrust $P_x \cdot a$ applied to opposite edges of length a provided that a is considerably longer than the wavelength of the folds which develop. The equation of Euler is:

$$P_x \leqslant \frac{8\,\pi^2 E\, h_0^3}{3(1-\sigma^2)\lambda^2}\ ;\ P_x \geqslant \frac{8\,\pi^2 E h_0^3}{3(1-\sigma^2)\lambda^2}(1-\sigma)^2 \tag{14}$$

where E is Young's modulus of elasticity, and σ is Poisson's ratio (see Prescott, 1946, p. 479).

Equations (13) and (14) show that the buckling thrust, per unit length in the direction parallel to the fold axis, is inversely proportional to the square of the wave length, all other conditions being constant. The wave length of a buckling plate consequently tends to be as large as the dimentions of the plate permit provided that the transversal movement of the buckles is not restricted by for example a surrounding viscous substance. For an unrestricted plate, then, its whole length will constitute one half wave; this gives maximum value of λ_i and minimum value of the buckling thrust. If transversal movement of the plate is restricted, however, it is possible that the plate can only respond to the thrust by forming several buckles with correspondingly smaller wave length. The necessary thrust force then increases rapidly with number of half waves or decreasing wave length.

DEFORMATION IN ENCLOSING VISCOUS MEDIUM DURING BUCKLING OF A PLATE

The viscous strain in the enclosing rock as caused by small-amplitude buckling of a vein may be treated with sufficient accuracy for our purpose in the following manner. Consider an imaginary column in the host rock with thickness dx extending from the convex side of the buckle to the distance z_e beyond which no distortion is noticeable in the host. The column is of unit width in the y dimension, figure 2.

The column has been compressed plastically an amount Δ. We shall assume that this strain has occurred at constant rate in unit time. The compressive strain, as well as rate of strain, has a maximum value at the contact of the plate and vanishes for all practical purposes at the distance z_e. For

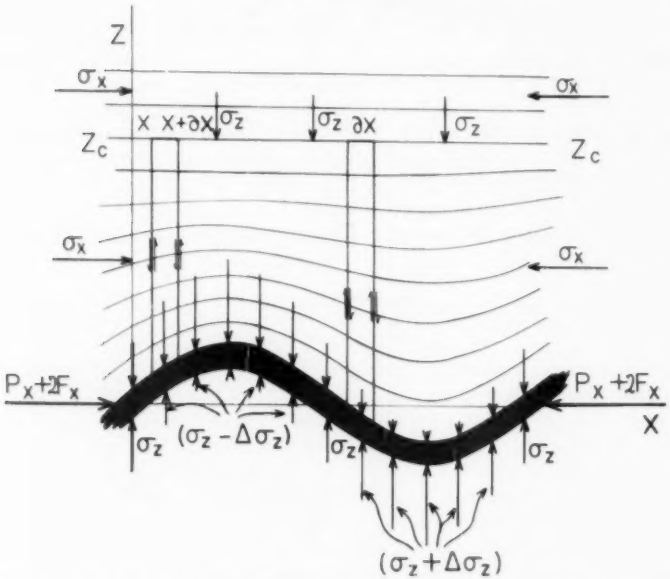

Fig. 2. Part of a folded "competent" rock-layer (black) enclosed in "incompetent" rock. The sinusoidal curves above the black layer were originally horizontal marker lines in the host rock which have been deformed. The depth of strain penetration is z_c. The deformation below the layer is not shown. $\sigma_z \pm \Delta\sigma_z$ are stresses imposed upon the buckling layer by the viscose resistance in the host rock. The compressive force $P_x + 2F_x$ is caused by compressive flow parallel to x in the host rock, and consequent drag along the competent buckling layer in regions to left and right of the figure.

simplicity the friction between buckled vein and host rock is neglected in this case. Assuming linear change of compressive strain[1] along the column, one finds that the strain at the contact is $\varepsilon_z = -\dfrac{2\Delta}{z_c}$. Under the condition of two-dimensional strain in x,z, and zero strain along y, this compressive strain corresponds to a compressive stress $-4\mu_2\dfrac{2\Delta}{z_c}$ where μ_2 is the coefficient of viscosity.

The shear strain parallel to z along the sides of the column at x and x_1 dx must now be considered. We shall assume that the shear strain also varies linearly from zero at z_c to a maximum value at the plate contact. As shown in figure 2 the shear along the side at x *resists* the compression by a force $z_c\mu_2\dfrac{1}{2}\dfrac{\partial z}{\partial x}$. Along the side at $x + dx$ the shear strain *supports* the compres-

[1] An exponential variation of strain with distance from the contact is a more reasonable assumption. However, the simpler model based upon linear strain variation appears to give sufficiently accurate conclusions as to the relation between wave length, thickness, etc.

sion of the column by a force $z_c\mu_z \frac{1}{2} \frac{\partial \left(z + \frac{\partial z}{\partial x} \partial x \right)}{\partial x}$ inasmuch as the strains have developed at constant rate in unit time. The sum of the shear forces acting on the column in z direction is consequently: $\frac{1}{2} z_c\mu_z \frac{\partial^2 z}{\partial x^2} \partial x$.

The total force, dF_z, acting parallel to z on the end of the column at the contact is then[2]:

$$dF_z = -\Delta\sigma_z dx = 8\mu_z \frac{\Delta}{z_c} dx - \frac{1}{2} z_c\mu_z \frac{\partial^2 z}{\partial x^2} dx, \tag{15}$$

where $\Delta\sigma_z$ is the difference between the stress on the convex contact of the active fold and the stress at the contact before folding starts. The latter is identical to the stress σ_z in the surroundings outside the contact zone, z_c, as indicated on figure 2.

The model of pure compression combined with simple shear parallel to z in the imaginary host-rock column is of course a simplifying approximation. The true deformation of the column involves relative thickening, mainly in its middle portions, and bending of its middle part away from the convex apex of the buckle in the competent layer. This simplifications, however, seems not to cause serious errors in the two important quantities we are seeking, *viz.* the depth of contact-strain penetration, z_c, and the initial wavelength, λ_i.

Substitution of $\Delta = \Delta_o \sin \frac{2\pi x}{\lambda}$, and $\frac{\partial^2 \Delta}{\partial x^2} = \frac{\partial^2 z}{\partial x^2} = -\frac{4\pi^2 \Delta_o}{\lambda^2} \sin \frac{2\pi x}{\lambda}$

in equation (15) gives:

$$dF_z = 2\mu_z \Delta_o \left(\frac{4}{z_c} + \frac{\pi^2 z_c}{\lambda^2} \right) \sin \frac{2\pi x}{\lambda} dx, \tag{16}$$

the integration of which from $x = 0$ to $x = \frac{\lambda}{2}$ gives the total force, F_z, acting on the convex side of a half-wave:

$$F_z = \frac{2\mu_z \Delta_o \lambda}{\pi} \left(\frac{4}{z_c} + \frac{\pi^2 z_c}{\lambda^2} \right) \tag{17}$$

Keeping wave length and amplitude constant while one differentiates eq. (17) with respect to z_c and equates to zero results in the value of z_c which corresponds to minimum value of the resistance force F_z:

$$\frac{dF_z}{dz_c} = \frac{2\mu_z \Delta_o \lambda}{\pi} \left(\frac{\pi^2}{\lambda^2} - \frac{4}{Z_c^2} \right) = 0, \qquad \text{hence:} \tag{18}$$

[2] F_z refers only to that part of the total force which is caused by the motion of the buckle into the surrounding substance. That is: if the buckle did not move into the adjacent substance F_z would be zero even if there is a compressive stress parallel to z. F_z is defined as positive for compression.

$$z_c = \frac{2}{\pi} \lambda. \tag{19}$$

That is, the depth of contact-strain penetration in the host material is $2/\pi$ times the wave length for small-amplitude folds. This value of z_c has been used in figure 2. Now because of the approximation made in the deformation model as discussed above, it is probable that the true depth of strain penetration is somewhat larger than the calculated one. [The reason for that is that the stresses connected with the strains which have been neglected become less with increasing z_c- value.] According to experiments, however, (Ramberg, 1959) and field observations (fig. 3) the true depth of strain penetration is not ap-

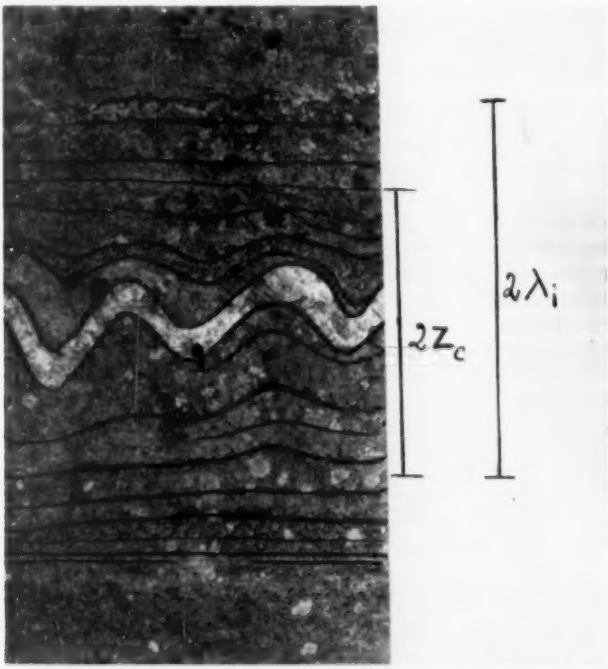

Fig. 3. Conformable ptygmatic quartz veinlet in micaceous quartzite. The layering in the quartzite and the boundaries of the vein are drawn in ink to show more clearly the contact strain. Note that depth of contact-strain penetration is less than the length of arc of one wave. (The vein is crossing the layering in the host rock at a very small angle).

preciably larger than the calculated value. Even for relatively large-amplitude folds such as in figure 3 we see that the strain does not extend as far as one initial wave length (= arc length of a wave) out in the host rock.

Incidentally, one notes that the contact strain depth is independent of the viscosities of layer and host.

In order to compare the resistance against folding as offered by the enclosing substance, with the buckling resistance, P_z, of the plate itself, the force F_z must be transformed to the equivalent force, F_x, acting in x direction along the folded sheet. This is accomplished by equating the moment of F_z acting on one fourth wave to the moment $F_x \Delta_o$:

$$(20)\quad F_x\Delta_o = M = \int_0^{\lambda/4} \Delta\sigma_z x dx = \frac{8\mu_2 \pi \partial\Delta_o}{\lambda\, \partial t} \int_0^{\lambda/4} x \sin\frac{2\pi x}{\lambda}\, \partial x = \frac{2\mu_2 \lambda\, \partial\Delta_o}{\pi \partial t},$$

where $z_c = \dfrac{2\lambda}{\pi}$ has been inserted. Δ_o – which is the amplitude developed with constant rate in unit time—has also been replaced by the general rate of amplitude growth: $\partial\Delta_o/\partial t$.

Substituting for Δ_o by equation (7), and for $\partial\Delta_o$ by $-\dfrac{\lambda\partial\lambda}{2\pi^2\Delta_o}$, eq. (9) gives:

$$(21)\quad F_x = -\frac{2\mu_2 \lambda^2\, \partial\lambda}{\pi(\lambda_i^2-\lambda^2)\partial t} = \frac{\mu_2 \lambda\, \partial\varepsilon_x}{\pi\, \varepsilon_x\, \partial t}, \text{ where } \partial\varepsilon_x = \frac{\partial\lambda}{\lambda},\quad \frac{\lambda_i-\lambda}{\lambda} = -\varepsilon_x,$$

and λ is very close to λ_i because we are only concerned with small-amplitude folds. The force due to strain in the enclosing substance on the convex side of a buckle equals very closely the force due to strain on the concave side (see fig. 2). The resistance offered by the enclosing substance on both sides of a buckle as expressed in terms of force parallel to x in the folded plate is then $2F_x$.

The total resistance against folding of the competent layer embedded in the incompetent medium is:

$$(22)\qquad F_s = P_x + 2F_x = \left(\frac{16\,\mu_1 h^3 \pi^2}{3\,\lambda_i^2} + \frac{2\mu_2 \lambda_i}{\pi}\right)\frac{\partial\varepsilon_x}{\varepsilon_x\, \partial t}$$

where μ_1 and μ_2 are the viscosity coefficients of competent layer and incompetent host substance respectively. h is half the thickness of the layer, and λ_i is initial wave length or length of arc of fold. P_x is given by equation (13).

As P_x decreases with increasing λ, and F_x increases with increasing λ, one may expect that the total resistance F_s has a minimum value for a given wave length. This will be the wave length which actually develops when folding starts. The initial wave length which represents minimum resistance is found if one differentiates F_s with respect to λ_i and equates to zero:

$$(23)\qquad dF_s = \left(-\frac{32\,\pi^2\,\mu_1 h^3}{3\,\lambda^3} + \frac{2\,\mu_2}{\pi}\right)\partial\lambda\, \frac{\partial\,\varepsilon_x}{\varepsilon_x\, \partial t} = 0;\ \text{i.e.}$$

$$(24)\qquad \lambda_i = 2\pi h \sqrt[3]{\frac{2}{3}\,\mu_1/\mu_2} = \text{length of arc of mature folds.}^3$$

[3] M. A. Biot (1957) has arrived at a similar equation by a quite different method. After submitting this paper for publication, Dr. John Rodgers kindly directed the author's attention to the important work by Goguel (1948) who developed a wavelength equation (p. 296-297) similar to that of the author.

It is interesting that neither rate of folding nor compressive force enter the expression for λ_1 if the condition $\mu_1 = \text{const.}$; $\mu_2 = \text{const.}$ is satisfied. For many solids effected by microcreep (*i.e.* flow at stresses less than the practical yield values) μ may well vary with magnitude of stress or with rate of strain. Under such circumstances initial wave length of compressed plates enclosed in

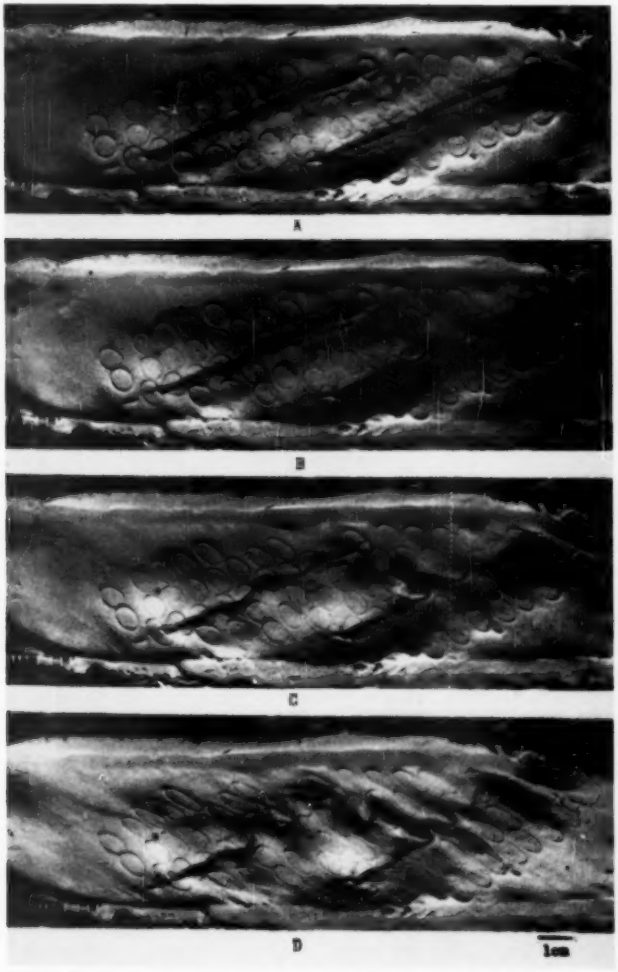

Fig. 4. Four steps in strain experiment with two layers of plasticene embedded in putty. The plasticene is about 100 times as viscose as the putty (order of magnitude). The layer on the left side with the longest wave length is somewhat thicker than the other. The strain was of simple-shear type with upper contact moved toward the left.

less viscose substances may depend on magnitude of compressive force and/or rate of strain.

Although the considerations above refer especially to folding of ptygmatic veins, it is obvious that they are applicable to plastic folding of "competent" rock layers in less "competent" host rocks in general as long as the boundary conditions are consistent with those assumed in this paper.

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ON THE ORIGIN OF THE CASPIAN AND BAIKAL SEALS AND THE PALEOCLIMATOLOGICAL IMPLICATION*

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ABSTRACT. The Caspian and Baikal seals, closely related to the ringed seal of the Arctic seas, are usually held to have arrived as a result of Pleistocene events. However, evidence suggests that they are relicts of late Miocene connections with the Arctic basin. The three species are more differentiated than is generally supposed. More important, some of the fossils from the upper Miocene of southern Russia and Hungary (and perhaps elsewhere) belong to the same subgenus (*Pusa*), and remains of the present Caspian seal are found in lower Pleistocene deposits, formed before the putative glacial entry of seals.

The fossils most readily diagnosed as belonging to the ringed seal group are an anterior fragment of a skull attributed to *Phoca pontica* by Alekseev and part of a lower jaw named *Praepusa pannonica* by Kretzoi. Some of the syntypes of *Phoca pontica* Eichwald (1853) also belong to this group and a lectotype is accordingly chosen here to prevent further confusion of the name. Much confusion has resulted from the identification by Simionescu as *Phoca pontica* of a form with a peculiar, distally expanded femur; this species is named *Pontophoca sarmatica* (Alekseev) n. comb. The synonymies of other forms which have been involved with the status of *Phoca pontica* are reviewed and lectotypes chosen when necessary.

The northern seals (subfamily Phocinae) are relatively cold stenothermic and probably entered the Sarmatian basin by direct connections to the north. The pups of living Phocinae have white coats as an adaptation to birth on ice, and this is almost certainly of common ancestry; the three species of the subgenus *Pusa*, within this subfamily, even more probably retain this adaptation from a common ancestor. Thus, if the ancestors of the Caspian seal were present in late Miocene times, ice almost certainly formed then, at least in the Arctic basin, and probably in the innermost reaches of the Sarmatian Sea.

INTRODUCTION

The presence in two great Asian lakes of seals closely related to the ringed seal of the Arctic seas has naturally excited much speculation. This note is prompted by certain Russian and eastern European papers which present views on the subject which are not widely recognized. Basically two theories have been put forward to explain the origin of these seals. The first presumes that they arrived as a result of Pleistocene events, and this is the only theory to be found in the zoogeographical literature of western Europe and America, as far as the author is aware. The second theory supposes that the Caspian seal and probably the Baikal seal are relicts of older, Tertiary connections with the northern seas. This paper attempts to show that the latter is the correct view.

The seals involved are members of the subfamily Phocinae of the hair seal group (family Phocidae). The systematics of the subfamily have been reviewed recently by Chapsky (1955a), whose views are substantially adopted by Scheffer (1958).

Many seals produce and nurture their pups on ice, but only the living members of the subfamily Phocinae (except for the specialized and probably early-separated bearded seal, *Erignathus*) are apparently derived from a single ice-breeding common ancestor. They are all related on anatomical grounds, of course, but more significantly their pups all have a white natal

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coat (lanugo). One, the harbor seal (*Phoca vitulina*) of the Atlantic and eastern Pacific, now breeds on land and the pup sheds the white coat *in utero*. The gray seal (*Halichoerus*) has turned to land-breeding in parts of its range, surely recently, for the pup retains the white coat. In all others the pup is produced on ice, where the functional value of the white coat is obvious in protective coloration and perhaps thermoregulation. It is improbable that this adaptation developed independently in seven species of the same subfamily. In the Antarctic, where predation (until man came) was not a factor, the white coat is not found in the five species of hair seal which may pup on ice. In the north Atlantic, the hooded seal (subfamily Cystophorinae) and the bearded seal (mentioned above) have failed to develop this feature. The importance of these considerations will become apparent.

The ringed, Caspian, and Baikal seals are members of the genus *Phoca*. Their subgenus, *Pusa*, has recently been raised to generic rank by Scheffer (1958), but reference to *Phoca* is preferred as it implies a relationship to the harbor seal group (*Phoca vitulina*) rather than to the other members of the subfamily Phocinae (the more specialized *Pagophilus*, *Histriophoca*, and *Halichoerus*). This follows the recommendation of Chapsky (1955a).

The Caspian seal (*Phoca caspica*) and the Baikal seal (*P. sibirica*) were described in 1788 by Gmelin, who thought them to be varieties of the harbor seal (*P. vitulina*). However, it became apparent that they were allied to the ringed seal (*P. hispida*), their affinities being discussed in detail by Nordqvist (1899), who relegated them to subspecific status. Seals have even recently (Mohr, 1952) been listed as possibly living in the Asian lakes Oron, Aral, and Kuku-nor, but this apparently is a mistake, for no seals are found in these lakes today (Ognev, 1935; apparently not noted by Mohr).

The possibility of Pleistocene origin will be discussed first. It will not be elaborated here in detail, since its refutation depends on confirmation of the opposing theory.

THE THEORY OF PLEISTOCENE ORIGIN

To account for the presence of Arctic elements, including the seal, a fish, and several Crustacea, in the Caspian Sea, Högbom (1917) assumed that a late glacial emigration from the Baltic region had occurred. The mechanism involved damming by glacial ice of northern lakes with the appropriate relict fauna, causing them to overflow into the Volga drainage and thence into the Caspian basin. Two of the relicts (the fish *Stenodus*, and the amphipod *Gammaracanthus*) are unknown from the Baltic or its relict lakes, and this led Pirozhnikov (1937) to propose that the northern fauna had been sent southwards from ice-dammed lakes formed by the west Siberian ice sheet.

Davies (1958a), who recently treated pinniped zoogeography as a whole, has accepted Pirozhnikov's theory and has attempted to elaborate and date the sequence of events. He supposes that during the third glaciation, which was the most extensive, the ice sheet formed first on the highlands of Novaya Zemlya and the Taimur Peninsula, spread southward to dam up the Ob and Yenesei Rivers, and picked up the seals from the gulfs of these rivers. The seals thus became inhabitants of the lake formed along the southern margin of

the Siberian ice sheet. There is geological evidence for a lake or lakes, which were controlled by a spillway at the head of the Tobol River and discharged into a route leading to the Aralo-Caspian basin (Flint, 1957). There is no evidence, however, for a lake as extensive as that which Davies has drawn (his figure 7, 1958a), incorporating the Caspian and Aral Seas and extending to the Central Siberian Highland. Lake Baikal drains into the Yenesei River, but is at present 300 meters above any possible ice-dammed lake. Davies cites evidence for considerable epeirogenetic uplift during the Pleistocene, and supposes that Lake Baikal would have been more accessible during the third glacial advance.

THE EVIDENCE FOR TERTIARY ORIGIN

The other opinion, that the Baikal and Caspian seals are relicts of pre-Quaternary connections of these waters with the northern seas, is not new. It was first put forward in the last century (by Andrussov, 1888; cited by Chapsky, 1955b), but only recently has the idea been given the full attention it merits by Chapsky, whose views form the basis for much of the argument presented here.

First of all, the degree of differentiation of the two lake-dwelling seals must be clarified. Nordqvist (1899) considered them to be subspecies, thus expressing their greater difference from the northern ringed seal than found in the "varieties" inhabiting the Baltic lakes Ladoga and Saima, which were obviously of recent, post-glacial origin. Subspecific status is still commonly accorded to them in the literature of northern Europe (Mohr, 1952; Eckman, 1953; Segerstråle, 1957) and this status would accord with a presumption of their Pleistocene origin. However, most recent authors concerned with their systematic position have given them specific status, if only because of their isolation.

The ringed seal of the Arctic and north-boreal seas is quite variable, and has been divided into a number of subspecies. Doubtless Scheffer (1958) is correct in presuming that most of these are invalid. At any rate, probably none can stand as defined, for the descriptions fail to account for differences imposed by age and sex (Chapsky, 1952) and for ecotypical differences in size related to ice conditions and latitude (McLaren, 1958). The differences between the ringed, Caspian and Baikal seals are not of this order at all and have been underemphasized. Chapsky (1955a; 1955b) redescribes each species thoroughly, but all their characteristics cannot be repeated here. There are consistent, age-independent differences in the skulls of the species. The pelt of the ringed seal throughout its wide range is "ringed" or marbled, that of the Baikal seal is spotted, while the skin of the Caspian seal is an unmarked gray. There are differences in parasites and feeding habits. There is a pronounced difference in the reproductive ecology of the Caspian seal, which breeds gregariously on ice floes, whereas the other two construct solitary pupping-lairs in the snow overlying land-fast ice.

The Caspian seal appears rather more differentiated from the ringed seal type, although the two lake seals have some features in common not found in the ringed seal. Taliev (cited by Brooks, 1950) found the Baikal seal serologi-

cally closer to the Arctic ringed seal than to the seals of Lake Ladoga or the Caspian Sea. However, this result cannot be significant of relationships, for there is no doubt that the Ladoga seal is merely a recently isolated and little differentiated ringed seal.

Taken as a whole, these differences imply an earlier separation than if we dismiss the inland seals as being mere subspecies of the ringed seal. Now an argument based on degree of differentiation alone would not suffice to overcome the argument for Pleistocene origin. The latter theory could claim that the populations were, at least on arrival, very small, and that this combined with the isolation in new surroundings would certainly result in more rapid evolution. However, the evidence for a pre-Quaternary origin of the Caspian seal, at least, rests on the fossil record, which must supersede any theory based on the Recent forms alone.

Pre-Pleistocene fossils.—The Sarmatian and Pontian basins of the late Miocene and early Pliocene[1] have provided a surprising number of fossils of marine mammals. Among the more important papers describing these fossils are those of Alekseev (1924a; 1924b), Kretzoi (1941), Macarovici and Oescu (1941), Macarovici (1942), and Simionescu (1926). Kellogg (1922) gives a very thorough review of all earlier finds, and Friant (1947) lists and discusses most species described to that date. Seals of the tropical-Antarctic group (subfamily Monachinae) and the northern group (subfamily Phocinae) are represented.

One of the first species described was *Phoca pontica* Eichwald (1853) from the Sarmatian of Bessarabia and from two localities on the Kerch Peninsula, both listed as Pontian (e.g., Kellogg, 1922), but apparently Sarmatian (Alekseev, 1924a). The name has become badly confused, for the original description was based on material of more than one species, and the name has since been applied to still other forms. Since the identification and relationships of *Phoca pontica* are important to the argument, it is necessary first to discuss misapplications and dubious changes of the name, and to divest it of fossils which are unrelated to Eichwald's type material. After this we may redefine the species from the original description by choosing a lectotype and then discussing its relationships. There are other problems of relationships and synonymy among the Sarmatian species, but these are beyond the scope of the present paper.

The fossils named *Phoca pontica* from Bessarabia were shown by Nordmann (1860) to be from a much larger species, which Nordmann renamed *Phoca maeotica*. There is complete agreement among the several authors on the identification of at least the femur (fig. 1e) of this large form, although it has been removed from the genus *Phoca* by some. Trouessart (1897) recognized that it belonged to the tropical-Antarctic group and renamed it *Monatherium maeoticum* (the spelling *Monotherium* has priority; see Kellogg,

[1] There is controversy over the correlations involved, but Russian workers (e.g., Neiman, 1957) believe that the Pontian stage and some of the top of the Sarmatian stage are to be considered as Pliocene. Some of the Sarmatian fossils have been listed as middle Miocene, but this cannot be maintained. It is sufficient for the argument and for wider correlation to suppose that the events described here took place near the Miocene-Pliocene transition. Reference has been made to the Lexique Stratigraphique International for correlation with western Europe.

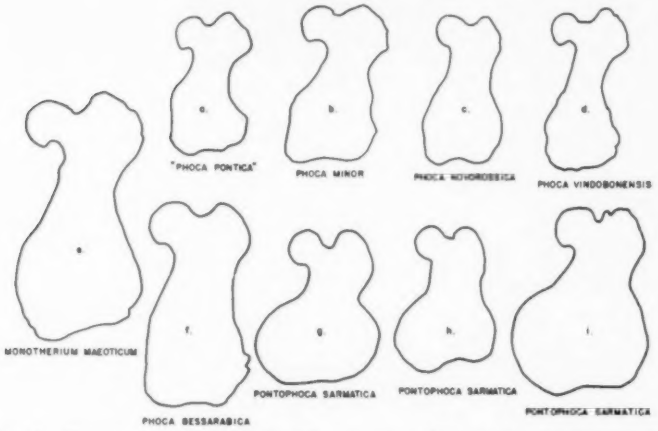

Fig. 1. Femurs from fossil seals. All to same scale (×1/3). Some reversed from originals for purposes of composition. (b and d from Friant, 1947; h from Simionescu, 1926; i from Macarovici and Oescu, 1941; others from type illustrations, as discussed in text.).

1922). The work of Nordmann should have resulted in the restriction of the name *Phoca pontica* to fossils from the small species of *Phoca* which formed important parts of the collection described, without designation of a holotype, by Eichwald.

Peters (1867) attributed seal fossils from the upper Miocene of the Vienna basin to *Phoca pontica*, without illustrating his material. Toula (1898) believed that these and more extensive remains were referable to a new species, *Phoca vindobonensis*.

Alekseev (1924a) described and figured from middle Sarmatian deposits of Kishinev the facial part of a skull and a fragment of a lower jaw, apparently from the same individual. These were from a small seal of the subfamily Phocinae and matched very well the small braincase from the Kerch Peninsula illustrated by Eichwald (1853) for *Phoca pontica*. Alekseev found skeletal material as well, which he neither described nor figured, but which he also referred to *Phoca pontica*.

Other bones, of which the femur seems to have been the source of most confusion, have been used to define the Sarmatian species. The femur (fig. 1a) considered to be part of the type of *Phoca pontica* by Eichwald was very small (65 mm. long) and resembles quite closely the femora of other species of *Phoca*, particularly *Phoca minor* (fig. 1b) from the Pliocene of Belgium, as illustrated by Friant (1947).

A grossly different form of femur (fig. 1h), with a very much expanded distal portion, was attributed to *Phoca pontica* by Simionescu (1926). Later Macarovici and Oescu (1941), following Simionescu, described a similar but larger femur (fig. 1i) under the same name. These are without doubt the same type of femur (fig. 1g) which had been defined earlier by Alekseev (1924b)

under the then new name *Phoca sarmatica*. Macarovici (1942), having newly discovered Alekseev's work, recognized this relationship and felt that the form described by Alekseev should be considered a variety, *Phoca pontica* var. *sarmatica*. Macarovici realized that these femora (fig. 1g, h, i) by no means matched the original illustration of the femur (fig. 1a) of *Phoca pontica*, but claimed that they fitted Eichwald's description of this bone. Actually, Eichwald's description agrees with his illustration quite adequately, and the measurements given in his text are exactly those of the illustrated femur. In the meanwhile Kretzoi (1941), who had not seen Alekseev's (1924b) work, recognized that the "*Phoca pontica*" of Simionescu (fig. 1h) had peculiarities which demanded its removal from the genus *Phoca*, and accordingly he renamed it *Pontophoca simionescui*. Friant (1947) had at hand an illustration of this peculiar femur which, following Simionescu, she believed to be representative of *Phoca pontica* Eichwald. Although apparently unaware of Kretzoi's work, she too recognized that this femur did not belong to the genus *Phoca*, and considered it to be allied to the modern tropical seal. Thus *Phoca pontica* Eichwald was termed *Monachus ponticus* (Eichwald) by Friant. In fact, this femur seems to bear little resemblance to that of the modern genus *Monachus*, or any other Recent genus. It is generically distinct and under the rules of priority it should retain the generic name given it by Kretzoi (1941) and the specific name given it earlier by Alekseev (1924b). It is therefore now designated *Pontophoca sarmatica* (Alekseev) McLaren n. comb. It is just possible that there are two types of seals involved under this name, in view of the wide range of size shown by the femora (fig. 1h, i), but the point to be made here is that they are not representative of, nor even related to the type material of *Phoca pontica*.

Macarovici (1942) also attempted to clear up confusion surrounding three other species of seals: *Phoca novorossica* Alekseev (1924b), *P. bessarabica* Simionescu (1926), and *P. vindobonensis* Toula (1898). In doing so, he reduced the second to synonymy with the first, on the basis of supposed resemblances of their femora and pelves. However, Alekseev stated emphatically that his *Phoca novorossica* was a small species, comparable in size with *Phoca vindobonensis* of the Vienna basin. *Phoca bessarabica*, as described by Simionescu and later by Macarovici and Oescu (1941), was a much larger form comparable in size with *Monotherium maeoticum*. The femora (fig. 1c, f) of the two forms that Macarovici considered synonymous actually bear little resemblance to one another and are respectively ca. 65 and 94 mm long. The pelves are more alike in appearance but show the same disparity of size. One might accept Macarovici's contention that size alone is not sufficient to separate these species, but at this point the status of *Phoca pontica* becomes involved. Since Macarovici had decided that the "real" *Phoca pontica* was represented by the peculiar femur discussed above (*Pontophoca sarmatica*), he concluded that the femur (fig. 1a) illustrated by Eichwald belonged to the species *Phoca novorossica* (fig. 1c), with which he considered *P. bessarabica* (fig. 1f) to be synonymous. There seems to be no justification for this identification of the femur originally described among the type material of *Phoca pontica*.

Kretzoi (1941) was unsatisfied with the supposed affinities of the femur and humerus illustrated by Eichwald as *Phoca pontica* and believed that they were referable to the Monachinae. He therefore proposed a new genus for the species and called it *Monachopsis pontica*, without designating a lectotype. No other worker seems to have considered this possibility, which appears unlikely as regards the femur at least, considering the small size of the bone and its resemblance to femora of other species of *Phoca*. The humerus is rather shorter and thicker than comparable bones from Recent *Phoca*, but these differences do not seem to be a sufficient basis for Kretzoi's new generic name.

Bogachov (1927) described a humerus from Sarmatian deposits near Baku on the Caspian Sea which was almost identical with that described by Eichwald among the type material of *Phoca pontica*.

Finally, Calvert and Neumayr (1880) have listed a few remains from Turkey which they believed were identifiable as *Phoca pontica*. Unfortunately, they gave neither measurements nor illustrations which would perhaps demonstrate the affinities of their finds, for at that time they seemed unaware of the possible existence of more than one species of seal in Sarmatian deposits.

There remains, then, the problem of redefining *Phoca pontica*, which has been cleared of some unrelated material, but which probably contained more than one species as described. For these reasons we must choose a lectotype from the type material of Eichwald (1853).

The fossils which were described in the original publication without designation of a holotype were all from the Kerch peninsula. Among them were a part of the cranium, a few teeth, some vertebrae, part of the sternum, a fragment of the scapula, the pelvic girdle, humerus, femur, radius, tibia, patella, some of the bones of the carpus and tarsus, and some phalanges. Eichwald mentioned the larger Bessarabian fossils, which later became *Monotherium maeoticum* (Nordmann, 1860), but these did not acutally enter into his description of *Phoca pontica*. Indeed, Eichwald thought that his fossil seal must have resembled closely the modern harbor seal, *Phoca vitulina*, and apparently used the skull of this living species as a model from which to outline the missing portions of his fossil skull. Thus we may take Eichwald's *Phoca pontica* as based on specimens from the small species of *Phoca* which were actually included in the collection which he described. Of those who have sought to define or rename *Phoca pontica*, Alekseev (1924a) was the first, and he alone has described further material (the anterior fragment of a skull) which has given us a more precise conception of this small species of seal and which agrees with at least part of Eichwald's type material. It is felt that the posterior part of the skull, well matched by the anterior part discovered by Alekseev (as shown here in fig. 2), should serve as the restricted type material, and it is therefore designated as the lectotype of *Phoca pontica* Eichwald. Other parts of the skeleton included in the original description are problematical. They were collected over a period of time from beds in two localities and we are given no information on which bones were found grouped together. For reasons which will be given later (p. 59) the first metatarsus illustrated by Eichwald can safely be placed in the same species as the skull. Although the femur appears perfectly suitable as part of a small species of *Phoca*, it has been the subject of so much controversy that it had best be excluded from

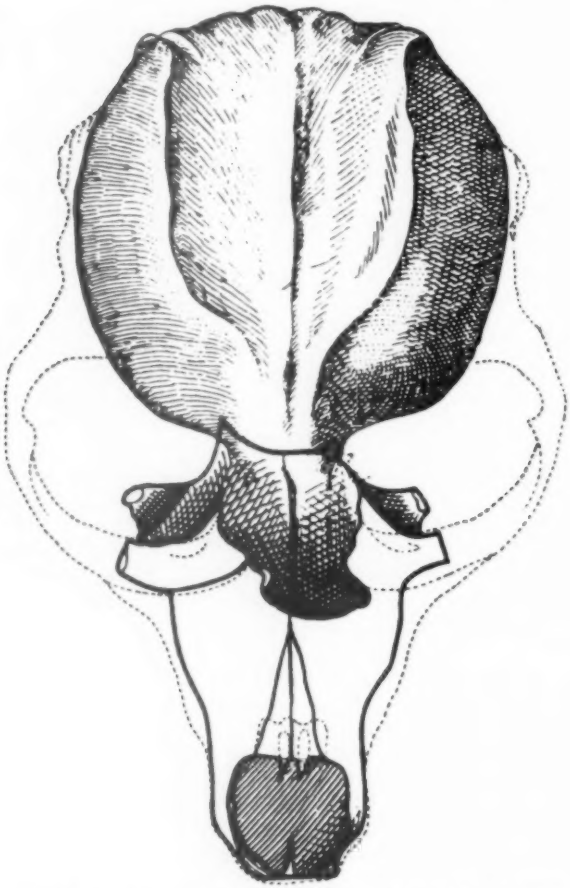

Fig. 2. The anterior fragment of the skull described by Alekseev matched with the posterior fragment illustrated by Eichwald (1853) as the type of *Phoca pontica* (×1). The dotted outline represents Eichwald's attempt to reconstruct the skull, using *Phoca vitulina* as a model. From Alekseev (1924a).

Phoca pontica for the present; the same is true of the humerus. Other bones should be referred to *Phoca pontica* only if they can be shown in future studies to belong to the same species of seal represented by the skull and first metatarsus.

Eichwald had supposed that the fragment of the cranium of *Phoca pontica* indicated close affinities with *Phoca vitulina*. In fact, the small size of the cranium which he has reconstructed, which is evidently from an adult, makes a relationship with the subgenus *Pusa*, or ringed seal group, far more likely.

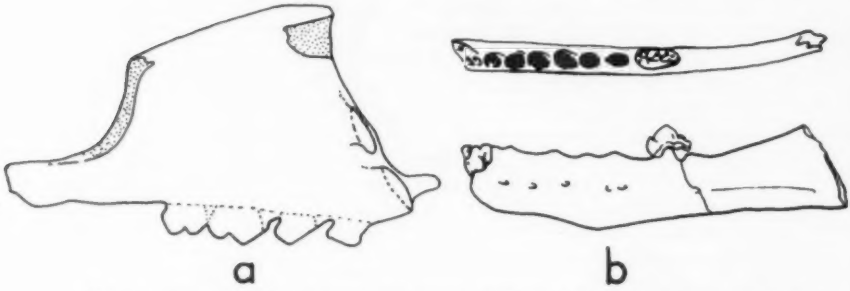

Fig. 3. Significant fossils from the upper Miocene (×1). At left (a) outline sketch from a photograph of the anterior fragment of the skull attributed to *Phoca pontica* by Alekseev (1924a). The teeth appear to be obscured by matrix in his photograph. At right (b) the lower jaw described by Kretzoi (1941) as *Praepusa pannonica*, as redrawn from his sketch.

The facial portion of the skull (outlined here in fig. 3a) which Alekseev (1924a) referred to *Phoca pontica* is most important. Alekseev compared it with skulls of *Phoca hispida*, *P. vitulina*, and *Pagophilus groenlandicus*, but did not ascribe it to any of these species. Although he found most points in

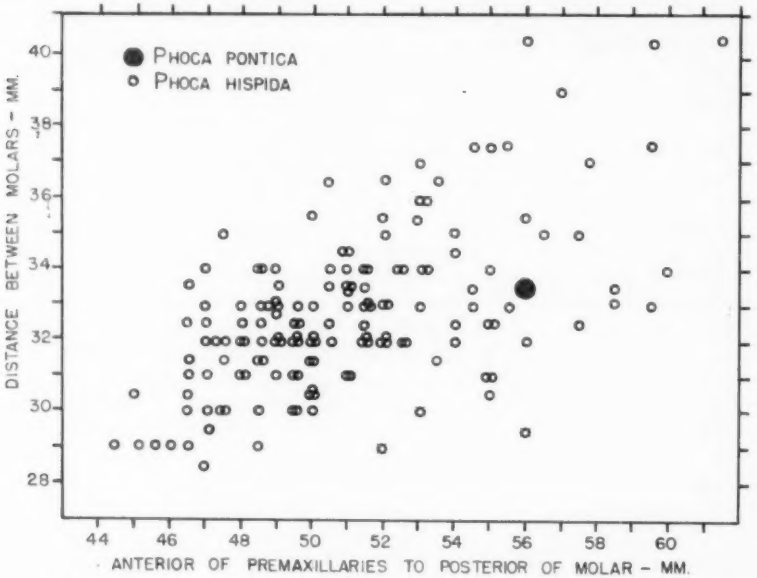

Fig. 4. Comparison of general form and size of the snout of *Phoca pontica* with the range shown by adult *Phoca hispida* (all aged at more than 7 years) from various localities in the Canadian Arctic. The distance between the molars (M_1) of *Phoca pontica* is listed by Alekseev (1924a); the distance from the anterior tip of the premaxillaries to the posterior margin of the molar was measured from his photograph.

common with *Phoca hispida*, he supposed that the muzzle was in general too elongate to resemble that of the living form. In fact, such elongation is typical of adult *Phoca hispida*. It is plain from figure 4 that Alekseev's specimen, here referred to *Phoca pontica*, does not differ from *Phoca hispida* in size or relative length of snout. A few years after Alekseev's study, Bogachov (1927) compared Alekseev's specimen with the equivalent part of the present Caspian seal and found many points in common. However, perhaps because he was misled by the skeletal material discussed above, it seemed impossible to Bogachov that *Phoca pontica* could be ancestral to the living form. Chapsky (1955b) has left no doubt that Alekseev's find belongs to the subgenus *Pusa* and the present author agrees completely with this conclusion.

The northern seals (Phocinae) can most readily be separated on the structure of the jaws and teeth, and Chapsky seemed unaware that Kretzoi (1941) had made a very significant find. Kretzoi described from middle Sarmatian deposits near Budapest a fragment of a mandible (fig. 3b) which is unquestionably of the subgenus *Pusa*, in view of its light structure and small last molar (the only tooth remaining). He was fully aware of its relationships and named it *Praepusa pannonica*. Since *Praepusa* has no characters separating it from *Phoca* (*Pusa*), Kretzoi's generic name must be changed to *Phoca*.

Bogachov (1927) believed that a humerus and a femur from Sarmatian deposits of the Caspian basin were referable to *Phoca vindobonensis* Toula (1898). These fossils were also noted as being very similar to the equivalent bones of the present Caspian seal, and Bogachov offered this as evidence of the late Miocene origin of the modern species. Chapsky (1955b) also stressed the resemblances between parts of *Phoca vindobonensis* and *P. caspica*.

Undoubtedly more of the bones of Phocinae described from Sarmatian deposits will prove to belong to the subgenus *Pusa*. In the author's opinion these fossils are best considered as marking a southward extension in the range of ancestors of *Phoca hispida*, which have since been isolated to give rise to the present Caspian seal. It seems unlikely that more than one species of this subgenus existed in Sarmatian waters, and while a conservative attitude must be taken at present, it is probable that fossils from this subgenus will be shown in future to be referable to *Phoca pontica*, as here restricted. Information is badly needed on the extent of variation of the limb bones of the living species in order that species may be more sensibly defined among the fossil seals.

The formal synonymy of the relevant species is summarized here. Lectotypes are chosen for all species in which a holotype was not designated and comments are offered on some of the referred material. Kellogg (1922) is the most useful source of further references, not involving the status of *Phoca pontica*, but concerning some of the listed species.

Subfamily Monachinae

Monotherium maeoticum (Nordmann)

Phoca pontica (p.p.) Eichwald, 1853.

Ph(oca) maeotica Nordmann, 1860.

Phoca maeotica Alekseev, 1924b; Simionescu, 1926; Macarovici and Oescu, 1941; Macarovici, 1942.

(*Monatherium*) *maeoticum* Trouessart, 1897.
Monotherium maeoticum Kellogg, 1922.
Monatherium maeoticum Friant, 1947.

Lectotype: The femur described and illustrated by Nordmann (1860, text p. 321, atlas pl. 23, figs. 8 and 9) as part of the type material.

Comments on referred material: According to Alekseev (1924b) the femur, humerus, radius, and pelvis in Nordmann's figures are attributable to this species, while the cubitus and the tibia belong to *Pontophoca sarmatica*.

Range: Lectotype from Sarmatian limestone in vicinity of Kishinev. Apparently confined to Bessarabian deposits.

Subfamily Monachinae?

Pontophoca sarmatica (Alekseev), n. comb.

Phoca sarmatica Alekseev, 1924b.
Phoca pontica Simionescu, 1926; Macarovici and Oescu, 1941; Macarovici, 1942.
Phoca pontica var. *sarmatica* Macarovici, 1942.
Pontophoca simionescui Kretzoi, 1941.
Monachus ponticus Friant, 1947.

Lectotype: The femur described and figured by Alekseev (1924b, p. 203, fig. 6) as part of the type material.

Comments on referred material: The humerus described and figured in the type material may belong with *Phoca bessarabica* according to Macarovici (1942). Other material acceptable as this species includes the femurs described as *Phoca pontica* by Simionescu (1926) and Macarovici and Oescu (1941).

Range: Precise locality of lectotype not given. Found in middle Sarmatian beds near Kishinev and also near Tsmiliansk on the Don River.

Subfamily Phocinae

Phoca (Pusa) pontica Eichwald

Phoca pontica (p.p.) Eichwald, 1853.
Phoca pontica Alekseev, 1924a; Kirpichnikov, 1953.
Phoca pontica (?) Bogachov, 1927. (See below).
Monachopsis pontica (?) Kretzoi, 1941. (See below).
Phoca novorossica (p.p) (?) Macarovici, 1942. (See below).
Not: *Phoca pontica* Peters, 1867.
Phoca pontica Simionescu, 1926; Macarovici and Oescu, 1941; Macarovici, 1942.
Phoca pontica var. *sarmatica* Macarovici, 1942.

Lectotype: The fragment of the cranium described and figured by Eichwald (1853, text p. 391; atlas pl. 13, fig. 1).

Comments on referred material: The metatarsus I of Eichwald's type material and the anterior fragment of the skull described by Alekseev (1924a) are safely referable to this species. Possibly also the femur illustrated by Eichwald, renamed *Monachopsis pontica* by Kretzoi (1941), and attributed to *Phoca novorossica* by Macarovici (1942). The humerus (also renamed as part

of *Monachopsis pontica* by Kretzoi and found in Caspian basin deposits by Bogachov, 1927) is problematical.

Range: Lectotype from upper (?) Sarmatian of Kerch Peninsula (Crimea), but precise locality not given. Other specimens were collected later from Sarmatian limestone near Kishinev and (possibly) from the Sarmatian of the Caspian basin near Baku.

The following are maintained as separate species, with the understanding that parts of any of them may in future be referable to *Phoca pontica* Eichwald or that synonymies may exist between them.

Phoca vindobonensis Toula

Phoca pontica Peters, 1867.
Phoca vindobonensis Toula, 1898, and all subsequent authors.
Phoca vindobonensis Bogachov, 1927.

Lectotype: The femur described and illustrated by Toula (1898, p. 62-63, pl. 2, fig. 2a, b, c) as part of the type material.

Comments on referred material: No problems of the affinities of the type material have been raised.

Range: Lectotype from Sarmatian near Vienna (Kreindl's brickyard on the Nussdorf road near Heiligenstadt). Since from Vienna basin and Sarmatian deposits near Baku, on the Caspian Sea.

Phoca novorossica Alekseev

Phoca novorossica Alekseev, 1924b; Friant, 1947.
Phoca novorossica (exclusive of parts belonging to *P. bessarabica*) Macarovici, 1942.
Not: Femur illustrated by Eichwald as *Phoca pontica* and referred to *Phoca novorossica* by Macarovici, 1942.

Lectotype: The femur described and illustrated by Alekseev (1924b, p. 203, fig. 10) as part of the type material.

Comments on referred material: Some parts of the type material may belong with other species according to Macarovici (1942). Although Macarovici thought the femur resembled that of *P. bessarabica*, this is not so (see fig. 1c and f here), and the femur is safely chosen as the lectotype. The small pelvis seems validly included with the femur of this species.

Range: Locality of lectotype not given. Found in Sarmatian of Bessarabia, Odessa, on the lower Dnieper River, and near Stavropol.

Phoca bessarabica Simionescu

Phoca bessarabica Simionescu, 1926; Macarovici and Oescu, 1941.
Phoca novorossica (p.p.) Macarovici, 1942.

Lectotype: The pelvis described and figured by Simionescu (1926, p. 187, pl. 2, fig. 1) as part of the type material.

Comments on referred material: Unfortunately, the femur had not been discovered when this species was described and the pelvis must serve as the lectotype. The femur was described and figured by Macarovici and Oescu (1941). Macarovici (1942) then reduced this species to synonymy with *P.*

bessarabica, but this is rejected here for reasons given above.

Range: Lectotype from middle Sarmatian limestone near Kishinev, and since only from that locality.

Phoca (Pusa) pannonica (Kretzoi)

Praepusa pannonica Kretzoi, 1941.

Holotype: As defined by Kretzoi (1941, p. 275, fig. 1), the fragment of a left lower jaw.

Comments on referred material: Kretzoi defined as paratypes the proximal and distal ends of the left tibia and the distal end of the left fibula.

Range: Type and paratypes from the lower middle Sarmatian (Ukrainium) of Erd, near Budapest (6 m. deep in Cerithian chalk on the property of Franz Bitter).

Pleistocene fossils.—Another form of paleontological evidence is the demonstration that seals very like the modern Caspian species were present during early Quaternary times. A fossil tibia, indistinguishable from the comparable bone of the present Caspian seal, has been described by Vershchagin and Gromov (1952) from a site on the Ural River, over 500 km. north of the shore of the present Caspian Sea. They could not give the precise stratigraphic position, but attempted to correlate it by indirect means with the Kvalinsk transgression of the Caspian Sea (last or Würm glaciation). This find cannot be adduced as evidence for a pre-Pleistocene arrival, for the proponents of Pleistocene origin suggest that the previous glaciation (third, or Riss) was responsible for the arrival of seals. It should be noted, however, that the Pleistocene fossils of ringed seals are in their turn indistinguishable from the modern species, *Phoca hispida* (see Kellogg, 1922).

A more significant fossil was described by Kirpichnikov (1953) from the south coast of the Sea of Azov, from deposits which are correlated with the Bakinsk transgression of the Caspian Sea of the early Pleistocene (second or Mindel glaciation). At this time the Black (Azov) and Caspian Sea basins were connected. The bone, a first metatarsal, was found in fluvial deposits, along with the remains of early Pleistocene terrestrial mammals (*Elephas meridionalis*, *Equus sussenbornensis*, etc.). Since the deposit contained redistributed fragments of the middle Sarmatian marine mollusc, *Cryptomactra pesanseris*, it had been considered possible that the seal bone was of Sarmatian age as well. However, Kirpichnikov rejects this conclusion by comparing the metatarsal with equivalent bones from one contemporary *Phoca caspica* and three upper Sarmatian seals referred to *Phoca pontica* (and wholly comparable with the first metatarsal illustrated by Eichwald, 1853). Indeed his measurements and figures do suggest that the fossil from the Sea of Azov matches best with *Phoca caspica*, but they also stress that there is very little difference between the metatarsal of the modern seal and those of the Sarmatian species. Kirpichnikov cites records of the entry of the present Caspian seal far into rivers as pointing to the way in which the fossil bone came to be found in fluvial deposits, along with remains of terrestrial mammals.

The evidence suggests, then, that a seal very like the modern Caspian seal was present in the Black Sea basin during early Quaternary times, before the

putative Riss glacial entry of seals into the Caspian Sea. Kirpichnikov does not concern himself with the possibility of genetic ties between the late Miocene seals and the modern form, but if his argument on the age of his fossil is disputed, the only alternative is that a seal very like the modern Caspian seal was present in the Black Sea basin during Sarmatian times, which has already been shown on other evidence.

Apparently other remains of seals (cited by Bogachov, 1927, Kirpichnikov, 1953, and Chapsky, 1955b) were found in the Bakinsk (lower Pleistocene) deposits of the Caspian Sea itself, but unfortunately these do not appear to have been compared with material from the Recent species.

If seals of the subgenus *Pusa* were thus present in Sarmatian waters, and if seals very like the present *Phoca* (*Pusa*) *caspica* were found there during early Quaternary times, then we must accept these as substantial refutations of the theory of later Pleistocene origin of the Caspian seal.

While there is no fossil evidence for the Baikal seal, it would be an economy of theory to explain their presence in the same way. We must finally fall back on the fact that the Baikal seal is more than slightly differentiated from the ringed seal.

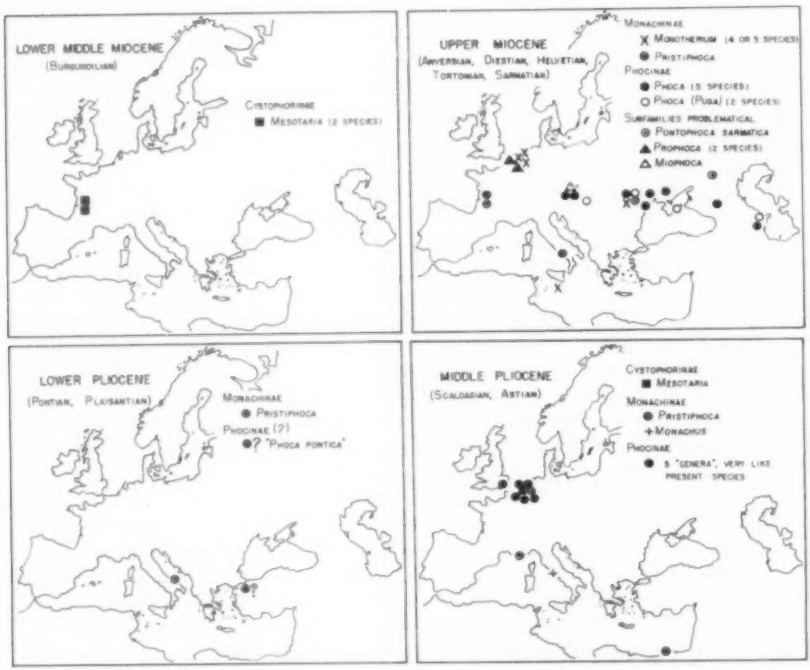

Fig. 5. Geographic and stratigraphic distribution of fossil seals in Europe. Each symbol represents a described species in each locality.

THE ROUTES OF ENTRY OF THE SEALS

It will be profitable to refer briefly to the overall fossil record (fig. 5). Although Cetacea are known earlier, the first fossils of seals in Europe are teeth found in the middle Miocene of southwest France. These are problematical, but are referred to the subfamily Cystophorinae (elephant and hooded seals).

Numbers of seals are described from the marine deposits of the upper Miocene, including those dealt with above. It can be noticed on figure 5 that, while the Sarmatian basin had several species of *Phoca* as well as seals of the tropical-Antarctic group, the Mediterranean and western European fossils are mostly of the Monachinae, except for a single femur from southwest France described as *Phoca coufloni* by Friant (1947) and two large hair seals (*Prophoca*), certainly not closely related to the modern northern seal group, from Anversian deposits.

The lower Pliocene has not produced much fossil material, but fragmentary remains from Turkey were referred to "*Phoca pontica* (see p. 53) and a seal (*Pristiphoca*) from Italy is close to the modern tropical seal (Friant, 1947, has in fact referred *Pristiphoca* to the genus *Monachus*).

In the middle Pliocene a whole host of species appears in the deposits of Belgium and Holland. One is of the Cystophorinae and one of the tropical-Antarctic group, while the others are "genera" (Friant, 1947, has reduced all but one to *Phoca*) quite close to the modern Phocinae. In the Mediterranean, the modern tropical seal was present.

Davies (1958b) has argued cogently for the origin of the Pinnipedia in the Arctic basin, and for the continuous restriction of the Phocinae to the northern hemisphere, by stressing the relative stenothermy of all except the Monachinae (all others live only in waters of less than 20°C maximum). There is little doubt that for the northern seal group during the late Miocene, the route around western Europe, through the Mediterranean, and into the Sarmatian Sea would have been too warm. The discovery of only one species of *Phoca* in deposits of that time in western Europe also suggests this (and *P. coufloni*, based on only one specimen, might bear re-examination). We must then consider a route of entry from the north.

Kretzoi (1941) saw no difficulty in connecting his *Praepusa pannonica* of Hungary with living seals of the same group, and with a zoogeographical flourish he created a "paratethys" in which the ancestral seals were developed. Along with two openings to the Arctic, one to the Mediterranean, and one to the Pacific, this Paratethys Sea was extended to cover Lake Oron, the Aral Sea, and Lake Kuku-nor, where no seals exist (p. 48). Kretzoi's Paratethys is purely imaginary, although his fossil find cannot be denied.

The northern shore of the Sarmatian Sea is difficult to restore with precision, since erosion has destroyed the deposits (Chapsky, 1955b). Although a connection between the Tethys Sea and the Arctic Ocean was present during early Tertiary, its existence during Miocene times seems problematical (Ekman, 1953). Nevertheless, it is felt that some connection must be invoked to get northern seals into southeastern Europe in the late Miocene. Seals are quite capable of moving into fresh water, and the connection need not have

been strictly marine. However, as well as the ringed seal group, other types of northern seals appear to have been present, including forms which may have resembled more the modern *Phoca vitulina* and *Halichoerus* (the jaw of *Miophoca vestuta* Zapfe is supposed by Chapsky, 1955a, to resemble that of *Halichoerus*). All in all, a fully marine connection seems more likely, although not absolutely necessary to the argument.

Probably the late Miocene marine transgressions, well known in Europe, extended either from the Arctic or from the Sarmatian Sea and brought the seals close to Lake Baikal. Certainly the fauna of this ancient lake, except for the seal and possibly an amphipod, has otherwise been isolated from marine invaders from a time earlier than late Miocene (Brooks, 1950). The Arctic ringed seal probably swims in and out of Nettilling Lake, Baffin Island, (see Manning, 1943) and the same capacity might have enabled the late Miocene seal to enter Lake Baikal, even if that lake were above sea level. Davies (1958) cites evidence for epeirogenetic uplift during Pleistocene, arguing that the entrance of the lake by the seal occurred during Pleistocene before that uplift; the same evidence might indicate that the lake was even more accessible in late Miocene.

In summary, the progenitors of the Caspian seal and probably of the Baikal seal can be considered to have arrived from the northern seas by connections, which were essentially marine, in late Miocene times.

THE IMPLICATIONS FOR PLEISTOCENE ZOOGEOGRAPHY

It can be seen that the demonstration of the probable Tertiary origin of the Caspian seal casts at least some doubt on the significance of the great Siberian ice-dammed lake as an agency in zoogeography. Certain Russian and western European authors have made wide use of this lake in their theories. Segerstråle (1957) used it to get an amphipod (*Pallasea*) into Europe during the third glaciation. All the northern elements in the Caspian Sea are explained by it (Pirozhnikov, 1937). Gur'ianova (1939) demanded that it be brackish for some zoogeographical purposes, and suggested that it has been concerned in establishing certain brackish water animals in North America as well. Perhaps a note of caution should be offered. Many of the relict species in lakes which have been analysed in the light of Pleistocene events are widespread (some Holarctic) and very successful. They are also geographically little differentiated, but this may reflect stability rather than recent isolation. It would be profitable to reexamine some of these species to determine whether they were established as fresh-water relicts before Pleistocene times in parts of their present range. This applies particularly to the presumed Pleistocene relicts of the Caspian Sea.

THE IMPLICATIONS FOR PALEOCLIMATOLOGY

As Chapsky (1955b) has pointed out, the presence of the progenitors of the Caspian seal in Sarmatian Seas implies that ice must have formed at that time. Actually, accepting the fossil evidence and its correlations does not absolutely necessitate that we believe ice formed in the Sarmatian Sea, but makes it almost certain that ice formed somewhere during that time, as the following arguments will show.

It might be argued, against all probability (see p. 48), that the white-coat pup arose independently in the several groups of the subfamily Phocinae. But the argument that it arose independently in the three closely related species of a subgenus within that subfamily is even more untenable. If one of this primitively ice-breeding group has lived continuously in the Caspian basin since late Miocene, then ice was almost certainly present somewhere at that time.

Although it seems more simple to suppose that the seals retained the ice-breeding habit in the Sarmatian Sea, it could be argued that they lost this habit when they spread into southern regions, where ice was not available. This has happened to different degrees in two modern species (see p. 48). The Caspian seal has lost the specialized relationship to fast ice shown by the ringed and Baikal species (see p. 49) and this might be taken as an indication of adaptation to periods when there was much less ice and snow than found today. It is also possible that the fossils of *Phoca pontica* from southern Russia are from seals which died far to the south of their breeding range. The modern Caspian species finds ice only in the north, although it migrates annually to the southern end of the sea.

In considering the climatological significance of the Monachinae, related to the modern tropical seals, it should be remembered that there were several types of Monachinae present, and that the modern group also includes four Antarctic species. The subfamily was quite likely Tethyan in origin, and their eurythermy may have permitted them to transgress the tropics during Miocene times, thence to colonize Antarctica (Davies, 1958b). Thus the admixture of fossils from the tropical-Antarctic and northern seals is not as paradoxical as it seems at first. Perhaps significant also are the facts that only near Kishinev is *Phoca pontica* found in the same locality with other seals, and *Phoca pannonica* is found alone. Unfortunately, the precise stratigraphic positions of many of the fossils are not given, but it is quite possible that seals of the subgenus *Pusa* were not strictly contemporaneous with seals belonging to the Monachinae.

There is also the problem of why only the Caspian seal of the several Phocinae present and none of the Monachinae should have survived to the present day. This can be attributed to post-Miocene climatic vicissitudes, and it is noteworthy that only the members of the ringed seal group normally keep open holes in the ice during an entire winter season, although other northern species may maintain holes briefly.

Other evidence can be brought forward to suggest that the climate of the late Miocene was sufficiently cool to form ice.

In the seas, there is evidence (in displacement of large boulders; Chapsky, 1955b) that ice was present in the Pontian Sea, at least. Ekman (1953) discussed the climatic deterioration in the Caribbean and elsewhere during Miocene. Today's marine temperatures were essentially reached in the Pliocene (the late Miocene was only a little warmer) on the west coast of North America (Durham, 1950).

MacGinitie (1958) has recently reviewed our knowledge of climate since the late Cretaceous, with special reference to the history of the floras of west-

ern North America. The late Miocene was certainly warmer than at present, although most of the southward migration of the forests was completed by that time. Climatic zonation certainly existed in late Miocene, and while the western United States seemed little influenced by polar air masses, MacGinitie suggests that winter conditions occurred and snow probably fell in the northwestern United States. The European floras seem to have been affected more by Pliocene cooling.

In conclusion, ice undobutedly formed in the northern seas and probably in at least the innermost reaches of the Sarmatian Sea during late Miocene. This emphasizes the statement of Barghoorn (1953) that

> the great trend of Cenozoic climate which culminated in Pleistocene glaciation began in the mid-Tertiary, probably more than 20 million years ago. Pleistocene glaciation itself . . . may then be regarded as a geologic and climatologic event the antecedents of which extend over a fair segment of recent geologic time and is not to be viewed as a sudden change in the history of the earth's climate.

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STUDIES IN THE SYSTEM Mn–O: THE Mn_2O_3–Mn_3O_4 AND Mn_3O_4–MnO EQUILIBRIA*

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ABSTRACT. As a first step in an investigation of phase relations in the system Mn–O, the equilibria

$$6\ Mn_2O_3 = 4\ Mn_3O_4 + O_2$$

and

$$2\ Mn_3O_4 = 6\ MnO + O_2$$

have been studied in the temperature intervals 845 to 1029°C and 1248 to 1562°C, respectively, and at O_2 partial pressures ranging from 0.21 to 1 atm. and from $10^{-3.08}$ to 0.21 atm. respectively. The conditions for coexistence of two crystalline phases in stable univariant equilibria are expressed as follows:

$$Mn_2O_3,\ Mn_3O_4 : \log p_{O_2} = 8.05 - 10100 \cdot 1/T$$

$$Mn_3O_4,\ MnO : \log p_{O_2} = 13.31 - 26000 \cdot 1/T$$

Exploratory runs in the solidus temperature region for the composition range between MnO and Mn_3O_4 indicate the presence of a eutectic at approximately 1540°C.

An explanation is offered for the poor agreement among previously published data on these equilibria.

INTRODUCTION

The system Mn–O is of considerable economic importance. In addition to the role of manganese as an alloying element, it acts as a deoxidizer (as well as desulfurizer) in the production of steel; the oxide formed constitutes a part of the slag, and this in turn may have a serious fluxing effect on the furnace refractories. Thus precise knowledge of the reactions of manganese with oxygen is fundamental to the chemistry of steelmaking. The use of manganese dioxide as a depolarizer in the common dry cell has also stimulated considerable interest in the Mn–O system. The fact that the United States produces only a small percentage of the manganese it needs has caused a great deal of attention to be devoted to the effective utilization of manganese, improved recovery from its ores (which are principally oxides) and the recovery of manganese from slags and low grade deposits. For a scientific investigation of all these problems, a knowledge of the system Mn–O is necessary.

Inasmuch as manganese occurs in different states of oxidation, many of the problems encountered in determining and illustrating phase equilibria in the system Mn–O are similar to those in Fe–O. The latter system was studied very thoroughly by Darken and Gurry (1945, 1946), and methods for describing such systems have been discussed in several papers emanating from our laboratories during the past few years (see for instance a paper by Muan, 1958).

A complete study of phase relations in the system Mn–O involves work at relatively high temperatures and over a wide range of O_2 partial pressures. We have selected temperature and O_2 pressure limits for our present study with the following considerations in mind. First, while the entire range of O_2 partial pressures from approximately 10^{-20} to 1 atm. is of interest, it is ex-

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perimentally easier to work at O_2 pressures in the upper part of this range. This is mainly because the high activity of manganese in oxide phases under strongly reducing conditions makes it difficult to find a crucible material in which to contain the samples. Therefore, the first step in our investigation was limited to O_2 pressures ranging from 1 atm. down to $10^{-3.66}$ atm. The temperature range for our study was also limited by practical considerations. The upper limit of approximately 1550°C is a temperature which can be conveniently reached in platinum-20 percent rhodium resistance furnaces, and the lower limit is that below which equilibrium cannot be reached within a "reasonable" period of time, say 1-2 weeks. With these chosen limitations in our investigation, we will be mainly concerned with the equilibria

$$6\ Mn_2O_3 = 4\ Mn_3O_4 + O_2$$

and

$$2\ Mn_3O_4 = 6\ MnO + O_2$$

as well as limited parts of the solidus temperature region in the composition range between MnO and Mn_3O_4.

PREVIOUS WORK

Numerous investigations have been reported in the literature dealing with various aspects of the chemistry of manganese oxides. However, nowhere does there exist a comprehensive account of the temperature-pressure-composition relations in the system Mn–O.

It is widely known that the oxides MnO, Mn_3O_4, Mn_2O_3 and MnO_2 exist as stable crystalline phases and can be converted from one to the other by suitable adjustments of temperature and O_2 partial pressure. It is also generally assumed that some of these oxide structures, notably MnO and Mn_3O_4, may exist over a range of compositions deviating from the stoichiometric ratios represented by the above formulas. However, an inspection of the quantitative data available for the various equilibria shows that discouragingly large discrepancies exist among these data. This may be partly a result of the fact that many of the equilibria have been estimated by addition and subtraction of heat of formation and entropy data, each of which has considerable limits of error, rather than by direct experimental observation of the equilibria in question. However, even data obtained by different authors using essentially the same technique are in very poor agreement. It is suspected that extreme difficulty in attainment of equilibrium in this system is the main reason for these discrepancies.

Compositions of Mn_3O_4 have been studied by Millar (1928), Le Blanc and Wehner, (1934), and Shomate (1943), and by Moore, Ellis and Selwood (1950). While Le Blanc and Wehner found the Mn_3O_4 to contain a considerable amount of excess oxygen over stoichiometric, the other investigators reported the Mn_3O_4 in air to contain essentially the amount of oxygen corresponding to the formula Mn_3O_4.

Le Blanc and Wehner (1934), as well as Moore, Ellis and Selwood (1950), also studied the MnO phase and concluded that the compositions varied with conditions of preparation, without giving any reliable quantitative data for the limits.

A structural transformation is known to take place in Mn_3O_4 in the temperature interval between 1100 and 1200°C. Southard and Moore (1942), on the basis of heat content data, estimated that the transition takes place at 1172±40°C. McMurdie and Golovato (1948) showed that the low temperature tetragonal form inverts to a high temperature cubic form. They found the transition to take place at 1170°C upon heating, but at temperatures as low as 1100°C upon cooling. Van Hook and Keith (1958) re-investigated this reaction recently and placed the transformation temperature at 1160±5°C.

Mn_2O_3 is also known to exist in at least two polymorphic forms, as pointed out as early as in 1934 by Dubois. One form, generally called α, has a "C" type cubic structure, while the other, generally called γ, has a cation deficient, tetragonal, distorted spinel structure. According to Mason (1943) the α form is stable relative to the γ form under all conditions. The γ form was not encountered in the present investigation.

The melting point of metallic manganese is 1244±3°C (from data compiled by Sully, 1955). Various "melting points" of MnO and Mn_3O_4 have been reported in the literature although these have little meaning unless the O_2 pressure of the atmosphere is specified. This is particularly the case with "MnO"[1], the "melting point" of which probably varies by several hundred degrees depending on the O_2 pressure used. Indications are, however, that the maximum temperature on the MnO liquidus curve is 1750°C or higher (White, Howat and Hay, 1934, Glasser, 1958). The melting point of stoichiometric Mn_3O_4 has been reported by Van Hook and Keith (1958) to be 1562°C, while v. Wartenburg and Prophet (1932) determined the melting point in air as 1560°C.

Temperatures for decomposition of Mn_2O_3 to Mn_3O_4 in air and at 1 atm. O_2 pressure have been reported by Meyer and Rötgers (1908), Saito (1927) and by Drucker and Hüttner (1927). These authors indicate that decomposition takes place at approximately 940 and 1090°C in air and at 1 atm. O_2 pressure, respectively. However, these temperatures represent those at which the decomposition proceeds at an easily observable rate rather than defining the equilibrium existence of the two crystalline phases Mn_2O_3 and Mn_3O_4, at these O_2 partial pressures. Coughlin (1954) has compiled free energy tables, based mainly on heat of formation and entropy data, that permit calculation of the Mn_2O_3–Mn_3O_4 equilibrium. On the basis of his data the temperatures of equilibrium coexistence of the two crystalline phases are approximately 1170 and 1280°C in air and at 1 atm. O_2 pressure, respectively.

Even greater discrepancies exist regarding the equilibrium between Mn_3O_4 and MnO. Coughlin (1954) has very ably compiled the data that seem to be most reliable. His free energy tabulations for MnO are based on the heat of formation data of Southard and Shomate (1942), the entropy measurements of Todd and Bonnickson (1951) and the high temperature equilibrium studies of Aoyama and Oka (1933). Uncertainties regarding the composition of the MnO used in the latter experiments detract from the reliability of the data for calculating the equilibrium between MnO and Mn_3O_4.

[1] This phase will be designated MnO in the present paper for sake of convenience.

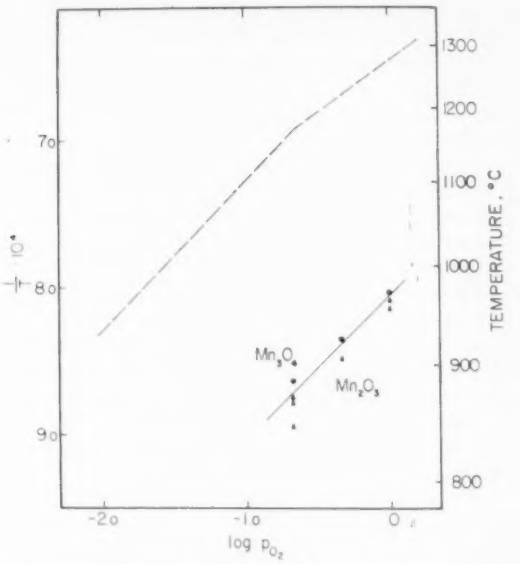

Fig. 1. Diagram showing the equilibrium relations of Mn_2O_3 and Mn_3O_4 as a function of O_2 pressure (log scale in atm.) and temperature (inverse °K scale). Solid triangles and circles represent observed stable occurrence of Mn_2O_3 and Mn_3O_4 respectively, and the solid line is drawn to fit the experimental data as well as possible. The dash curve is drawn to represent the same equilibrium on the basis of data tabulated by Coughlin (1954).

EXPERIMENTAL METHOD

General procedure.—Subsolidus equilibria were investigated by making runs at selected temperatures and O_2 partial pressures. Two samples, either Mn_2O_3 and Mn_3O_4 or Mn_3O_4 and MnO, were equilibrated side by side in the furnace. After a suitable time, determined by experience, the samples were quenched and the phases present determined by x-ray methods. In addition, runs were made in a thermal balance which permitted a direct observation of weight changes and hence the approach toward equilibrium as oxygen was added to or subtracted from the samples by reaction with the gas phase.

Charges for the investigation of solidus relations in the composition range between MnO and Mn_3O_4 were prepared by mixing various proportions of the two oxides. These charges were sealed in platinum-20 percent rhodium tubes, equilibrated in the furnace and quenched in water. The samples were then polished and examined microscopically under reflected light to determine the phases present.

Control of atmosphere.—The method used for controlling O_2 pressures was essentially the same as that used by Darken and Gurry (1945), and later by Muan (1955). Runs at 1 atm. O_2 were made by passing commercial tank oxygen through the furnace. Runs at 0.21 atm. O_2 were made by opening the

bottom of the furnace tube to allow air to circulate through. Runs at other pressures in the range $1\text{-}10^{-2.00}$ atm. were made by mixing O_2 and CO_2 in required proportions. In these cases the partial pressure of O_2 is determined directly from its partial pressure in the mixture at room temperature because at these concentrations of O_2 the dissociation of CO_2 can be neglected. Runs at lower O_2 partial pressures were made in CO_2 and in an atmosphere obtained by mixing CO_2 and H_2. The partial pressures of O_2 in these cases were calculated from the data compiled by Coughlin.

The gases used were of reported compositions 99.5 percent O_2, 99.956 percent CO_2, and 99.5 percent H_2. It was found necessary to remove O_2 from the CO_2 by passing the gas over copper gauze heated to 500°C.

The rate of flow of each of the two gases was measured separately by two capillary flow meters with bleeder tubes on both ends of the capillaries to maintain a constant pressure drop. A series of mutually interchangeable capillaries of different openings was at hand, so that a wide range of mixing ratios could be obtained with manometer readings of convenient magnitude. A third manometer was inserted in the line to measure the rate of flow of gas through the furnace. The flow meters were calibrated individually with the various capillaries, using a standard wet test meter.

Furnaces and temperature control.—Vertical tube furnaces with platinum-20 percent rhodium resistance windings were used throughout this investigation. The furnace used for the quenching experiments was provided in the upper end with a brass head through which sample holder or thermocouple protection tube could be inserted and clamped in gas tight connection. The lower end of the furnace was provided with a gas inlet device which permitted quenching of the sample without disturbing the atmosphere in the furnace. The gas escaped through a side arm attachment in the upper part of the furnace tube, and was passed through a bubbling bottle before going to the atmosphere.

The furnace used for the thermal balance experiments was equipped with ground glass joints fused to the top and bottom of the furnace tube. The upper glass attachment was drawn out to a long, relatively narrow tube to prevent air from diffusing into the furnace. In this furnace a sample could be suspended from an analytical balance by means of a fine platinum wire leading through the opening for the gas outlet. The approach to equilibrium could then be followed by weighing the sample periodically.

The furnace temperatures were regulated by means of control couples connected in the case of one furnace to a Celectray controller and in the other to a Brown Pyr-O-Vane controller. The thermal gradient at the hot spot did not exceed 2°C over 1 inch at 1400°C in either furnace.

Temperatures were measured before and after each run with a platinum-90 percent platinum 10 percent rhodium thermocouple. This was calibrated periodically at melting points defined as follows: Au, 1063°C; $CaMgSi_2O_6$, 1391.5°C; $CaSiO_3$, 1544°C. The tables compiled by Shenker, et al. (1955) were used for temperature interpolations.

Starting materials.—All oxides of manganese used in the present investigation were made from "Baker Analyzed" reagent grade manganese dioxide of reported analysis as follows: Assay (MnO_2), 100.0%; Fe, 0.020%; in-

soluble in HCl, 0.015%; chloride, 0.002%; nitrate, 0.050%; sulfate, 0.040%; earths and alkalies (as SO_4), 0.015%. Starting materials were made by igniting this oxide in air at approximately 800°C to produce Mn_2O_3 and at approximately 1100°C to produce Mn_3O_4. The MnO used as starting material was prepared by heating of MnO_2 at approximately 1100°C in an atmosphere with a CO_2/H_2 mixing ratio of approximately 10. In accordance with the results of Le Blanc and Wehner (1934) it was found necessary to cool the MnO in the furnace atmosphere to prevent the formation of higher oxides.

Chemical analysis.—The oxides were analyzed by determination of "excess oxygen", i.e., weight percent oxygen in excess of that corresponding to stoichiometric MnO. Approximately 0.1 gm of the oxide sample and 0.75 gm of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were added to 25 ml of H_2O, 10 ml of 1:4 H_2SO_4 and 3 ml of 49 percent HF, and the solution was allowed to boil for 10 minutes to dissolve all the sample. Upon cooling to room temperature 25 ml of distilled water and 15 ml of 2 percent boric acid were added and the solution was titrated with 0.05-normal $KMnO_4$. The value of the equivalents of excess oxygen was calculated as the difference between the equivalents of ferrous iron added and that reacting with $KMnO_4$. The addition of HF was necessary in order to avoid the difficulty encountered by Siemonsen (1939) in dissolving samples of Mn_3O_4 which had been prepared at high temperatures. Boric acid was added to complex the iron in order that the faint pink color of the end point in the titration with $KMnO_4$ could be observed. The $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ had to be standardized under the conditions of the analysis each time analyses were made because it will lose or gain water on standing.

Preliminary tests were made to determine whether the oxygen of the air affects the analytical results as it does in the use of the arsenate method as discussed by Stalzer and Vosburgh (1951). Duplicate samples boiled in air and in CO_2 gave identical results within limit of experimental error.

RESULTS

The composition of Mn_3O_4 in air and in 1 atm. O_2 was determined over the temperature interval from about 1100 to 1500°C. In preliminary experiments, starting samples of MnO and Mn_3O_4 were equilibrated side by side in the furnace until the compositions of both samples were the same. This was done at a high temperature and at the lowest temperature in the interval concerned. Once the time necessary to reach equilibrium at these two chosen temperatures had been determined, it was assumed than any run at intermediate temperatures would require no longer time to reach equilibrium than at the lowest temperature. Also, in succeeding runs only Mn_3O_4 was used as starting material. It was found necessary to quench these samples in water, for air quenching caused results which were inconsistent because of the reaction of the samples with the oxygen of the air upon cooling. The results of these runs appear in table 1.

The phase transformation in Mn_3O_4 occurs rapidly, and the high temperature form cannot be quenched to room temperature. It is inferred, however, that although the structure of Mn_3O_4 changes upon quenching, the composition does not change appreciably. The basis for this inference is that

TABLE 1

Analyses of Samples of Mn_3O_4 Produced at Different Temperatures in Air (pO_2 = 0.21 atm.) and at pO_2 = 1 atm.

	Temperature (°C)	Starting Material	Duration of Run (hours)	% Excess Oxygen (duplicate analyses)		Value of x in Calculated Formula (MnO_x) of Oxide	
				#1	#2	#1	#2
Runs in Air:	1099	MnO	40	6.94	6.97	1.331	1.332
	1099	Mn_3O_4	52	6.99	7.00	1.333	1.334
	1252	Mn_3O_4	43	6.93	6.96	1.330	1.332
	1393	MnO	53	6.98	7.03	1.333	1.334
	1393	Mn_3O_4	39	6.91	7.03	1.329	1.335
	1463	Mn_3O_4	34	6.90	—	1.329	—
	1535	Mn_3O_4	54	6.85	6.96	1.326	1.329
Runs at pO_2 = 1 atm.:	1085	Mn_3O_4	41	6.85	7.07	1.326	1.337
	1251	Mn_3O_4	72	6.95	6.94	1.331	1.331
	1383	Mn_3O_4	94	6.83	6.85	1.325	1.326
	1456	Mn_3O_4	36	6.87	6.91	1.327	1.329
	1505	Mn_3O_4	38	6.92	—	1.330	—

Saito (1927) and Meyer and Rötgers (1908), who followed the decomposition of MnO_2 on continuous heating in air by means of a thermal balance, found no abrupt change in weight in the vicinity of 1160°C.

Inasmuch as all compositions of Mn_3O_4 determined in the present investigation were in the range $MnO_{1.326}$ to $MnO_{1.334}$ and there was no systematic variation with temperature or O_2 partial pressure, it is concluded that the composition of this phase is essentially constant, corresponding to that of stoichiometric Mn_3O_4, under the conditions of temperature and O_2 pressure used in this investigation. Additional evidence of the constancy of composition was obtained in the present investigation by means of the thermal balance arrangement. A sample of Mn_3O_4, weighing approximately 1 gm, was equilibrated for two days in air at 1348°C. It showed no change in weight at the end of 17 hours after the atmosphere was changed to oxygen at 1 atm.

The equilibrium between Mn_3O_4 and Mn_2O_3 was investigated at 1 atm. O_2 pressure, in air, and in an atmosphere of intermediate O_2 partial pressure. The data for the critical runs appear in table 2. These data are plotted in figure 1 along with the values of log pO_2 calculated from the data compiled by Coughlin (1954). The value for the heat of reaction for the process $6Mn_2O_3 = 4Mn_3O_4 + O_2$ as calculated from the data of the present investigation is 46,200 ± 3,300 cal. The equilibrium decomposition temperatures of Mn_2O_3 to Mn_3O_4 as determined in the present investigation are 968 ± 5°C in oxygen at 1 atm. and 877 ± 8°C in air.

Data for the equilibrium between Mn_3O_4 and MnO appear in table 3. These data are plotted in figure 2 along with the values of log pO_2 calculated from the data compiled by Coughlin (1954). The high temperature limit of the experimental curve is that at which a liquid phase develops, as described later. The low temperature limit of the present investigation was the temperature of the Mn_3O_4–MnO equilibrium in pure CO_2. The mixing ratios,

TABLE 2
Critical Runs for Determination of the Equilibrium
$6Mn_2O_3 = 4Mn_3O_4 + O_2$

	Temperature (°C)	$1/T \cdot 10^4$	Duration of Run (hours)	Phase Present at Equilibrium
Runs in Air:	845	8.95	61	Mn_2O_3
	865	8.79	60	Mn_2O_3
	870	8.75	98	Mn_2O_3
	874	8.72	244	no change in either sample
	885	8.64	47	Mn_3O_4
	972	8.03	43	Mn_3O_4
Runs at p_{O_2} = 0.46 atm.:	905	8.48	308	Mn_2O_3
	924	8.35	288	Mn_3O_4
Runs at p_{O_2} = 1 atm.:	955	8.14	46	Mn_2O_3
	964	8.08	65	Mn_2O_3
	972	8.03	86	Mn_3O_4
	1029	7.68	42	Mn_3O_4

CO_2/H_2, necessary to obtain partial pressures of O_2 in the vicinity of the curve at lower temperatures would have to be greater than 500/1. In the case of such mixtures, serious doubts concerning the accuracy of the gas mixer would arise.

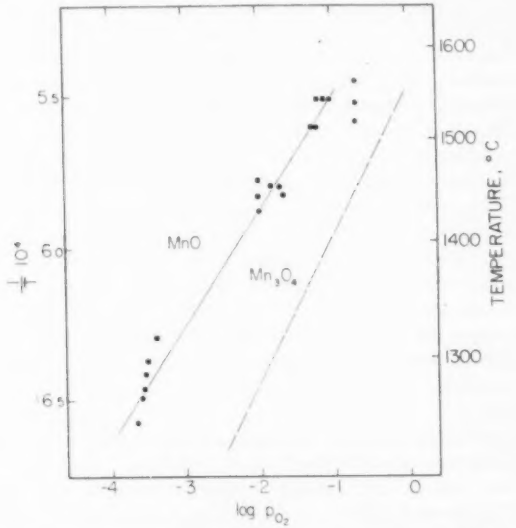

Fig. 2. Diagram showing stability relations of the phases Mn_3O_4 and MnO as a function of O_2 pressure (log scale in atm.) and temperature (inverse °K scale). Solid dots and squares represent observed stable occurrence of Mn_3O_4 and MnO, respectively, and the solid straight line is drawn to fit the data as well as possible. The dash straight line represents the equilibrium curve as calculated from data tabulated by Coughlin (1954).

The value of the heat of reaction for the process $2Mn_3O_4 = 6MnO + O_2$ as calculated from the data of the present investigation is 118,500 ± 2,500 cal.

Runs in sealed 80 percent platinum 20 percent rhodium tubes with mixtures intermediate in composition between MnO and Mn_3O_4 permitted the determination of lowest liquidus temperatures in this region. An invariant situation (eutectic) exists at 1540 ± 6°C with Mn_3O_4, MnO, liquid and gas present together in equilibrium. The O_2 partial pressure of the gas phase is determined as the intersection between the 1540°C isotherm and the MnO—Mn_3O_4 equilibrium curve in figure 2; the value is approximately 0.1 atm.

DISCUSSION

The compositions of the Mn_3O_4 phase determined in the present investigation agree well with those found by Shomate (1943) who prepared Mn_3O_4 by heating manganese dioxide in air to 1050°C, and Millar (1920) as well as Moore, Ellis and Selwood (1950) who prepared Mn_3O_4 by heating manganese sulphate in air at about 1000°C. Their results along with the calculated values for stoichiometric Mn_3O_4 are as follows (compare data in table 1):

	Percent excess oxygen	Value of x in calculated formula (MnO_x) of oxide	
Calculated	6.99	1.333	
Shomate	7.00, 7.01	1.334	1.334
Millar	7.01, 7.03	1.334	1.335
Moore, Ellis and Selwood	7.0	1.33	

In contrast to these results, the data of Le Blanc and Wehner (1934) indicate the existence of a Mn_3O_4 phase with considerable excess oxygen over stoichiometric in the temperature interval 400-500°C.

The melting temperature of Mn_3O_4 in air, 1567 ± 4°C, as determined in the present investigation, as in fair agreement with the value of 1560°C found by v. Wartenberg and Prophet (1932). It is also worth noting that Van Hook and Keith (1958) reported a melting temperature of 1562°C for stoichiometric Mn_3O_4 prepared by mixing MnO_2 and powdered manganese in the correct proportions and heating in tubes that were assumed to be gas tight.

The data for the reaction between Mn_2O_3 and Mn_3O_4 reported in the present paper we believe represent true equilibrium conditions, as distinguished from most data previously reported in the literature. We succeeded in attaining equilibrium in both directions, equilibrating samples of Mn_2O_3 and Mn_3O_4 as starting materials side by side and keeping them in the furnace up to two weeks.

The discrepancies between our data on this equilibrium and those of previous workers can probably be ascribed mainly to this difficulty of obtaining equilibrium. Meyer and Rötgers (1908), who reported decomposition temperatures of 940 and 1090°C in air and at 1 atm. O_2, respectively, stated specifically that the phase changes they observed were not reversible, but proceeded only from Mn_2O_3 to Mn_3O_4. Therefore, the decomposition temperatures reported by them were those at which the reaction took place in a "reasonable" period of time rather than true equilibrium values. Many other investigators, e.g., Saito (1927) and Drucker and Hüttner (1927), have confirmed or ap-

proximated the temperatures determined by Meyer and Rötgers. Unfortunately, some of these later investigators have failed to appreciate the significance of the reservations made by Meyer and Rötgers regarding the lack of equilibrium conditions. The transformation temperatures determined in the present investigation are also significantly lower than the values of approximately 1280°C at 1 atm. O_2 pressure and 1170°C in air calculated from the data of Coughlin (1954). The reasons for this discrepancy cannot be checked because Coughlin has omitted certain sources for the data which he has compiled for Mn_3O_4. However, in the light of the previous discussion concerning the transformation temperatures as reported in the literature, it can be suspected that if an experimentally determined transformation temperature was used by Coughlin in compiling his data, it was too high.

The ΔH° value of 46,200 ± 3,300 cal. for the reaction

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

determined in the present investigation (for the temperature interval 845-1029°C) agrees well with the value of 44300 ± 13600 cal. calculated from the data compiled by Coughlin.

An observation which was made during study of the Mn_3O_4—MnO equilibrium deserves special discussion. In preliminary experiments for determination of the equilibrium between Mn_3O_4 and MnO, the transformations of MnO to Mn_3O_4 and vice versa were studied under conditions of constant temperature and O_2 partial pressures which were later found to be well within the regions of stability of the respective oxides. These transformations were followed by means of the thermal balance and x-ray examination. The complete transformation in both directions took place in three to four hours in tests run at 1300°C. (The transformations were called complete when the sample had reached a constant weight and the quenched sample consisted of only one phase according to x-ray analysis.) It was later discovered that when the two starting materials, MnO and Mn_3O_4, were run simultaneously in the furnace at combinations of temperature and O_2 partial pressure representing conditions near the boundary curve on the MnO side (see fig. 2), both quenched samples turned out to be mixtures of MnO and Mn_3O_4 as determined by x-ray analysis. In other words, each of the phases (MnO and Mn_3O_4) seemed to be unstable with respect to the other—apparently a contradictory situation.

Experience showed that if both quenched samples were a mixture the first time they were removed from the furnace, the amount of the MnO phase increased and the amount of the Mn_3O_4 phase decreased in every case upon further time in the furnace at the same temperature and O_2 partial pressure. On the basis of this observation it was assumed that MnO is the truly stable phase under the conditions of O_2 partial pressure and temperature which resulted in this anomalous behavior of the samples.

Inasmuch as the composition of Mn_3O_4 is known to remain essentially constant and the composition of MnO has been reported to vary considerably (Le Blanc and Wehner, 1934), it is suspected that the MnO phase is the cause of the difficulty encountered near the boundary conditions. Exsolution of Mn_3O_4 from the oxygen-rich MnO phase near the boundary curve during quenching may be thought of as a cause of the anomalous observation dis-

cussed above. However, indications are that the observed phenomenon instead is related to the complex kinetics of the transformation of an MnO phase of one composition to another. It is important to note that the MnO used as starting material in these runs was made up under conditions of temperature and O_2 partial pressure which are known to be far removed from the conditions in which MnO is in equilibrium with Mn_3O_4. Runs in the thermal balance furnace showed that the weight of the MnO sample under these boundary conditions first increased rapidly, then remained essentially constant for a long period of time before finally decreasing. This observation together with the fact that x-ray analysis of quenched samples showed decreasing amounts of Mn_3O_4 with increasing time of equilibriation strongly suggests that MnO of low oxygen content first transforms partly to Mn_3O_4 before reacting with oxygen of the atmosphere to form MnO of higher equilibrium oxygen content at the conditions near the boundary curve. This problem will be dealt with in more detail in a later paper.

The heat of reaction for the process

$$2Mn_3O_4 = 6MnO + O_2$$

determined in the present investigation, 118,500 ± 2,500 cal., (in the temperature interval 1248-1540°C) does not agree well with the value of 94800 ± 1500 cal. calculated from the data compiled by Coughlin (1954). This, however, may be mainly an apparent discrepancy caused by differences in composition of the MnO phase involved in the reaction.

TABLE 3

Critical Runs for Determination of the Equilibrium

$2Mn_3O_4 = 6MnO + O_2$

Temperature (°C)	$1/T \cdot 10^4$	$\log p_{O_2}$	Duration of Run (hours)	Phase Present at Equilibrium
1248	6.58	−3.66	47	Mn_3O_4
1267	6.49	−3.59	22	Mn_3O_4
1274	6.46	−3.56	40	MnO
1286	6.41	−3.54	17	MnO
1297	6.37	−3.51	15	MnO
1315	6.30	−3.38	22	MnO
1429	5.88	−1.99	70	Mn_3O_4
1443	5.83	−1.99	22	MnO
1444	5.82	−1.66	26	Mn_3O_4
1453	5.79	−1.70	17	Mn_3O_4
1453	5.79	−1.82	20	MnO
1458	5.78	−1.99	72	MnO
1512	5.60	−1.20	17	Mn_3O_4
1512	5.60	−1.26	10	MnO
1517	5.59	−0.68	17	Mn_3O_4
1538	5.52	−0.68	11	Mn_3O_4
1542	5.51	−1.03	23	Mn_3O_4
1542	5.51	−1.10	7	MnO
1542	5.51	−1.10	9	MnO
1562	5.45	−0.68	7	Mn_3O_4

SUMMARY

Equilibria among the phases Mn_2O_3, Mn_3O_4 and MnO have been investigated as a first step in a study of phase relations in the system Mn—O. The investigation was limited to the temperature interval 845 to 1562°C and O_2

partial pressures ranging from $10^{-3.66}$ to 1 atm. The equilibria were studied mainly by the quenching technique, using microscopic, x-ray and chemical analysis for identification of phases in the quenched samples. These experiments were supplemented with weighing experiments carried out in a thermal balance setup.

Runs of long duration permitted equilibrium to be reached in both directions for the reaction

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

The temperature of equilibrium coexistence of Mn_2O_3 and Mn_3O_4 in air is 877 ± 8°C and at 1 atm. O_2 pressure 968 ± 5°C. The ΔH° for the reaction above as calculated from the data of this investigation is 46,200 ± 3,300 cal.

The composition of Mn_3O_4 was found to be essentially constant and equal to that of the stoichiometric formula at all temperatures studied (1085 to 1535°C) in air and at 1 atm. O_2 pressure.

The equilibrium between Mn_3O_4 and MnO according to the equation

$$2Mn_3O_4 = 6MnO + O_2$$

was studied in the temperature interval 1248 to 1562°C. A curve representing the equilibrium coexistence of these two crystalline phases as a function of temperature and O_2 partial pressure has been obtained. The ΔH° for the reaction as calculated from the data of this investigation is 118,500 ± 2,500 cal.

Exploratory runs in the solidus temperature region showed that an invariant situation exists in the Mn–O system at approximately 1540°C., with the following phases present together in equilibrium: Mn_3O_4, MnO, liquid and a gas phase with an O_2 partial pressure of approximately 0.1 atm.

During the study of the Mn_3O_4–MnO equilibrium it was observed that MnO used as starting material and equilibrated under conditions of temperature and O_2 pressure in the stability field of the MnO phase, but close to the Mn_3O_4–MnO boundary curve, upon quenching to room temperature gave a mixture of Mn_3O_4 and MnO (as revealed by x-ray examination). It is tentatively suggested that this phenomenon is related to the complicated reaction kinetics for transformation of a MnO phase of one oxygen content to another rather than a simple exsolution of Mn_3O_4 from the MnO phase during quenching.

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REVIEWS

The Fossil Book: *A Record of Prehistoric Times*; by CARROLL LANE FENTON and MILDRED ADAMS FENTON. P. 428, illus. New York, 1958 (Doubleday and Co., $12.50).—Continuing their work of presenting geology for the popular audience of older children and adults, the Fentons have explored the field of paleontology in this new volume. Written for the interested student of high school age—and equally fascinating to the adult layman—*The Fossil Book* is one of the best and most comprehensive non-technical books on this subject.

Beginning with introductory definitions of the nature of fossils, the scale of geologic time, and a brief discussion of stratigraphy, the first part of the book also includes a chapter on classification and principles of nomenclature. This information is all too often omitted from popular treatments of paleontology—particularly those prepared for this audience—and its inclusion here is therefore especially welcome. The discussion of fossil invertebrates as well as the more familiar vertebrates is also unusual and will extend the usefulness of the book.

The illustrations, both photographs and line-drawings, are excellent. Among the best are the many diagrams of comparative structures and the series of sketches of the Brachiopoda. For the amateur fossil-hunter these, together with the descriptions of collecting localities throughout the text, will undoubtedly make the book serve as a field guide as well as a library reference. The color plates are strikingly good and one might only wish that more of them could have been included.

In other respects, *The Fossil Book* is a work that can really be used. One of the best chapters is titled "Read, See, and Collect." It comprises an annotated list of the museums in this country that display fossils (including some of the smaller college and university museums which do not maintain public exhibits but will permit the use of their study collections); a good bibliography of suggested readings in general historical geology, as well as more specific fields; and finally a brief section on collecting techniques and equipment. There is also a glossary of terms and an index, which gives a pronunciation guide to scientific words used in the text.

Although the book is very well organized and equally well-written, it suffers from the inclusion of some questionable and inaccurate material. The geologic time scale is presented in a version not in common use today, as the detailed division of the Pre-Cambrian implies far more knowledge about this part of geologic time than most geologists assume, and would therefore be misleading to the student. The discussion of radioactive dating contains an outright error in its reference to radioactive isotopes of "zircon."

Paleobotany is discussed in two chapters, but it is unfortunate that in a work that aims at being inclusive more space is not given to this subject. The text would also have benefited from a fuller discussion of the significance of paleontology in extending our knowledge of evolution. While this is implied, it is not clearly stated, nor is evolution itself discussed in any detail, although much space is devoted to evolutionary histories.

Despite its shortcomings, *The Fossil Book* will be a much-needed addition to the shelves of many school, public, and individual libraries. Although its price may put it beyond the reach of many readers, it contains a great deal of up-to-date information, not usually brought together in a popular book written so that young people as well as adults can understand and enjoy it.

LYNNE SALISBURY

Principles of Geochemistry, 2d ed.; by BRIAN MASON. P. x, 310; 48 figs. New York, 1958 (John Wiley & Sons, Inc., $8.50).—The second edition retains the original organization of the book and most of the changes in the new edition are in the form of addition of new material rather than revision of the original text. The most marked changes are those concerning dating, isotope geology and phase equilibria.

Chapter 5 (Magmatism and Igneous Rocks) and Chapter 10 (Metamorphism and Metamorphic Rocks) have undergone most change. Chapter 5 now includes revised data on the phase relations of feldspars and pyroxenes and data on some mineralogical system recently investigated under various H_2O pressures. Chapter 10 incorporates a discussion of the sillimanite-kyanite-andalusite relations and the effect of H_2O and CO_2 pressures on the stability of various phases during metamorphism. It also includes a diagram of equilibrium curves for some significant metamorphic reactions at different temperatures and pressures. The whole section on mineralogical transformations and the facies principle has been revised to take account of this new data.

The changes in the other chapters are less extensive. These include accounts of the hypotheses of Urey and Hoyle on the origin of the universe and of Rubey and Urey on the origin of the atmosphere. The data on cosmic abundances, the age of the earth and the abundance of trace elements in various rock types have been revised. Additional diagrams are incorporated such as the one showing the relation of sedimentary mineral associations to Eh and pH. All the chapters have bibliographies which are expanded and brought up to date.

Thus the scope and purpose of the original book remain the same. The changes involved are only those necessary because of the accumulation of new data and the introduction of new theories during the six years since the publication of the first edition.

MICHAEL H. CARR

Publications Recently Received

Nature and Man's Fate; by Garrett Hardin. New York, 1959 (Rinehart and Co., $6.00).

Dana's Manual of Mineralogy, 17th ed; revised by Cornelius S. Hurlbut, Jr. New York,

Blakeslee: The Genus Datura; by Amos G. Avery, Sophie Satina and Jacob Rietsema. New York, 1959 (The Ronald Press Co., $8.75).

Lectures on Fourier Integrals; by Salomon Bochner (translated by Morris Tennenbaum and Harry Pollard. Princeton, 1959 (Princeton University Press, $5.00).

Chrystal Chemistry of Simple Compounds; by E. S. Makarov (translated by E. B. Uvarov). New York, 1959 (Consultants Bureau, Inc., $5.25).

The Chemical Elements; by Helen Miles Davis. Washington, D. C., 1959 (Science Service, 50 cents).

Our Mineral Resources; by Charles M. Riley. New York, 1959 (John Wiley and Sons, Inc., $6.95).

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